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An Investigation of the Role of the Adhesive in the Structure of Pigment-Adhesive Films

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AN INVESTIGATION OF THE ROLE OF THE ADHESIVE IN THE STRUCTURE OF PIGMENT-ADHESIVE FILMS

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SUMMARY

Much of the work which has been reported in the literature on paper coating film structures and film properties dependent upon film structure has been based upon the assumption that pigments pack independently of an adhesive, or that an adhesive ideally fills voids in a predetermined pigment skeleton. The hypothesis of the idealized filling of voids by an adhesive has been the only attempt at describing the relationship between a pigment and an adhesive during film formation. The goal of this thesis was to evaluate this hypothesis and thereby to establish the role of the adhesive in film structural formation.

The hypothesis of idealized void filling was evaluated for three pigment-adhesive systems by examining the effects of changes in adhesive contents on film specific volumes. Films from all three systems (starch-clay, PVA-clay, and latex-clay) were formed on a nonporous substrate, and films from one system (starch-clay) also were formed on a porous substrate. Techniques were developed for isolating film samples from the substrates upon which they were formed, and a technique was developed for measuring the specific volumes of films of any adhesive-to-pigment ratio. More detailed information on the effects of the adhesive upon film structures was obtained by applying the tools of x-ray diffraction, gas adsorption, and electron microscopy.

The results of this study showed that the hypothesis of idealized void filling was not valid for any of the pigment-adhesive systems considered. Each of the three adhesives combined uniquely with the same pigment to form widely differing film structures at equivalent adhesive levels. Initial amounts of the starch adhesive caused an expansion of the pigment skeleton of films which continued until a maximum expansion was reached. Further increases in starch content then led to a compaction of the pigment skeleton until a continuous starch-clay film was obtained. The PVA adhesive exhibited a similar trend in behavior, but caused a

maximum expansion of the film pigment skeleton at a much lower adhesive level than the starch. The latex adhesive continually expanded the pigment skeleton of latex-clay films until a continuous film was obtained, but the degree of skeletal expansion was much less than with the starch and PVA adhesives. The porous substrate markedly influenced the degree to which the starch adhesive affected film structure.

Mechanisms, which were consistent with the experimental results obtained, were proposed to explain the means by which each of the adhesives studied could have affected film structural formation. It was proposed that the starch and PVA adhesives affected the structural formation of starch-clay and PVA-clay films, respectively, by polymeric bridging of the clay particles at lower adhesive levels, and then at higher adhesive levels by acting as lubricants, and through the forces arising from the molecular packing of the adhesive polymers during film drying. It was proposed that the latex influenced film structure through the mechanical interaction of the latex and clay pigment particles during the formation of a latex-clay film. Finally, it was suggested that substrate porosity influenced the effect of the starch on film structural formation by changing the rate of film formation.

INTRODUCTION

The coating of paper and paperboard with pigment coatings has become an important segment of the paper industry. Pigment coatings are used to mask or improve the appearance of a sheet, to give opacity to a sheet, and to provide an improved printing surface (1). In addition, a pigment coating may be used to provide a special functional surface on a paper such as is required for certain duplicating processes. Pigment-coating films may contain a number of different types of pigment, the most widely used being kaolin clay.

In addition to the pigment, the coating film also contains an adhesive material. The main purposes for including an adhesive in the coating are to bind the pigment particles together within the coating film and to bond the film to the paper substrate. The types of binders used vary from natural polymers, such as colloidal starch and casein systems, to the many synthetic polymers available as solution or emulsion systems.

The majority of coating studies have concentrated upon the improvement of the commercially important end-use properties of the coatings, which include such things as pick strength, opacity, gloss, ink receptivity, and printability. These efforts have met with considerable success, as is indicated by the improvement in paper coatings over the years. Now, however, a more fundamental understanding of paper coating technology is needed to assure continued improvement in the properties of coated paper.

There are many factors involved in the pigment coating of paper and, obviously, an extensive study of all of these factors would not be feasible at this time. Therefore, this thesis has focused upon the function of the adhesive component in pigment coating. The literature in both investigative and patent form concerning the adhesives used in pigment coating is voluminous. However,

most of this information deals with the attainment of various desirable end-use properties within pigment coatings by the manipulation of the quantity and type of adhesive used with a given pigment. There is little or no explanation offered as to why or how these adhesives combine with pigments to produce films of varying properties. It is hoped that the study presented in this thesis will lead to a clearer understanding of the relationship between adhesives and pigments in paper coating films.

BACKGROUND TO THE PROBLEM

A pigment (or pigment-adhesive) coating consists of a pigment, or pigments, bound together by an adhesive to form a rigid, porous film structure on top of a paper substrate. The term structure, as applied to a coating film, refers to the arrangement of the pigment and adhesive components within the film, and may be described or defined in terms of various physical characteristics including density, surface area, pore volume, pore size distribution, and the alignment of the pigment particles relative to one another.

Many of the end-use properties of the pigment coating are predetermined by the structure of the pigment-adhesive film. For example, variations in the surface areas and pore distributions of coatings may affect changes in measured opacity (1). Ink receptivity may be a function of the pore size distribution and the total pore volume of a coating (2). The strength of a coating film is generally considered to be a function of the distribution of the adhesive within the pigment matrix as well as a function of inherent adhesive strength. This distribution of adhesive is thought to be related to measurable film surface area (3), pore size distribution within the film (4), and the arrangement of the pigment particles within the film (5).

Early studies on coating structures concentrated upon the measurement of some of the physical characteristics of films, as enumerated above, which were thought to be related directly to coating end-use properties, and very little work was undertaken to explain how film structures evolved to yield these particular characteristics. For example, Carson (6) and Tollenaar (7), who were interested primarily in ink receptivity and printability of coated papers, used permeability techniques to roughly describe the size of pores present in the coatings on selected grades of printing papers. However, they had no means of

explaining how the pore size distributions which they observed in their samples had come about. It soon became evident that to control the physical characteristics of a coating film and thus predict and improve coating end-use properties, an understanding of the manner in which a pigment and an adhesive combined to form a coating film structure was necessary.

Several workers have studied the packing characteristics of pigments from the point of view that such studies could lead to a complete understanding of the coating structure and properties of pigment-adhesive films. Cobb (8) was among the first to take this approach in her study of pigment adhesive demand. She reached the conclusion that, for a given pigment coating system, the strength of a coating film was related directly to the percentage of interpigment voids which were filled with adhesive material.

Cobb (8) assumed that the calculation of the percentage of voids filled by an adhesive could be based upon the void volume present when a water dispersion of a pigment was applied to a surface and subsequently dried with no adhesive present. She states, "when both pigment and adhesive were thus structurally considered on a volume basis, coating adhesive demand was found to be governed by the percent voids originally present in each pigment, as packed by the surface tension of the water used as test medium." Cobb has thus assumed that in coating film formation the pigment packs independently of the adhesive present, or that the adhesive simply fills predetermined void spaces in a pigment skeleton. The data which Cobb obtained for various casein-pigment coating systems seemed to support her hypothesis that an adhesive ideally filled pigment skeletal voids.

Shortly after Cobb's publication on pigment adhesive demand, Willets and Marchetti (9) reported their work on attempts to explain various coating end-use properties, such as pick strength and gloss, in terms of volume relationships

between pigments and adhesives in coatings. They determined what they felt was the critical pigment volume concentration (C.P.V.C.) for each of the pigment coating systems with which they worked. The C.P.V.C. was defined as the level of pigmentation in a dried coating film at which there was just enough adhesive present to fill the voids between the pigment particles. It was stated that this property of C.P.V.C. for a given pigment system was of particular significance as a measure of the void space between pigment particles in coating films formed using that particular pigment system.

Based upon void volumes for their various pigment coating systems as determined from C.P.V.C. measurements, Willets and Marchetti interpreted their experimental results to confirm Cobb's relationship between void volume and pigment adhesive demand. The assumption implied in this work was the same as that advanced by Cobb, namely, that coating film structures are determined primarily by the packing of the pigment, and that the pigment packs independently of the adhesive present.

Hagemeyer (10,11) has done extensive work on the packing characteristics of pigments. In his studies, variations were made in particle size, shape, chemical composition, and in combinations of these variables. In some cases, idealized mixtures of large, visibly different particle shapes were studied to observe the packing configurations. In all of this work the assumption was made that if the packing of the particles from an adhesiveless water system could be described, the information obtained would apply directly to a coating system.

Kraske (3) and Eames (4) in their studies on coatings did not claim that a pigment packed independently of the presence of an adhesive, but they did show that changes in pigment characteristics, such as size which affect pigment packing, did affect coating film structures and properties. Kraske (3) found that changes

in the size of the clay pigment component of a starch-clay coating film caused important changes in the measurable structural characteristics of surface area, pore size distribution, and clay platelet alignment within the film. Eames (4) found that the size of clay particles in starch-clay films was related to film strength.

The concept of idealized adhesive void filling of a predetermined pigment matrix has been used as a base for both planning investigations and interpreting experimental results on paper coatings. Robinson and Linke (12), in a recent study on determining the opacity of pigment-adhesive films, planned their experimental program on the basis that idealized void filling would occur in the pigment-adhesive system which they considered. Several investigators (13,14) in comparing the properties of pigment coatings containing different binders, such as starch and polyvinyl alcohol, have assumed that the same interpigment space exists no matter what the level or type of adhesive present. Thus, differences in film properties among films containing different adhesives were explained in terms of the percentage of interpigment space filled by the adhesives.

Paper coating researchers are not the only investigators who have made the assumption that a pigment packs independently of the adhesive present. Workers in the field of paint technology, who have long considered pigment-adhesive films on a volume basis, have had an interest in determining the critical pigment volume concentration (C.P.V.C.), which was defined earlier, for various paint systems. Early work on the determination of the C.P.V.C. for paint systems was considered unsatisfactory because the values obtained were not for dried paint films, but rather, for fluid paint colors (15,16). More recent efforts at determining the C.P.V.C. for paint systems have attempted to determine values for dried paint films, and into each of these methods (17-19) is incorporated the assumption that above the C.P.V.C. (the paper coating range), the pigment packs independently

of the adhesive. The experimental results of these investigations on the C.P.V.C. of dried paint films seemed to confirm the assumption of idealized adhesive void filling of a pigment matrix above the C.P.V.C.

In summation, the only available description of the arrangement or relationship between the pigment and the adhesive in a paper coating film is based upon the hypothesis of idealized adhesive void filling. If this concept is valid, many fundamental implications regarding coating films could be investigated. For example, the efficiency with which adhesives develop coating film strength could be compared as a function of inherent adhesive film strength. All adhesives would distribute themselves in the same manner in a given pigment skeleton, and thus differences in coating film strength would be due only to inherent strength differences between adhesives. In addition, for a given adhesive, the measurement of coating film surface area would be related to the bonded area, and thus strength of a pigment-adhesive film. Properties such as ink receptivity would be proportional to the volume of adhesive present to fill in a coating film pore structure.

However, if the assumption of adhesive void filling does not describe the relationship between the adhesive and the pigment in coating films, further use of that assumption in future coating studies will be fruitless. It will be necessary to develop new concepts concerning the effects of adhesives on pigment-adhesive structures and resulting film properties.

STATEMENT OF THESIS PROBLEM

Previous work on the formation of pigment-adhesive coating film structures has concentrated upon the packing characteristics of pigment particles, and the assumption has been made that a pigment packs independently of an adhesive, or that the adhesive simply fills voids in a predetermined pigment skeleton. The aim of this thesis is to evaluate this hypothesis of idealized adhesive void filling, and thereby establish the role of the adhesive in film structural formation.

The specific objectives of the study are:

1. What does an adhesive do, i.e., does it merely fill predetermined voids in a pigment skeleton, or is it a factor in establishing the skeleton?

2. Do adhesives differ with regard to formation of pigment-adhesive films? Do they distribute themselves in the same manner in a pigment skeleton, or does each adhesive combine uniquely with the same pigment to form <u>different</u> structures?

3. What effect does the substrate have upon the structural formation of a pigment-adhesive film? The substrate is one of the many factors which may affect film structure, and has been singled out for consideration here because it is felt that it may be the variable which interacts with the adhesive to the greatest degree during film formation.

APPROACH TO THE THESIS PROBLEM

The problem now becomes one of an approach to evaluating the hypothesis of idealized void filling and determining how an adhesive contributes to pigment-adhesive film structures. In order to do this, some theory on pigmented films was borrowed from the field of paint technology. Paint workers have long been concerned with the concept of the critical pigment volume concentration. In his work on the determination of the critical pigment volume concentration, Pierce and Holsworth (19) assumed the hypothesis of idealized void filling for pigment concentrations above the C.P.V.C., and thus developed mathematical expressions relating the specific volumes of films to film composition, both above and below this value. Their treatment, which follows, has been used in this study as a model system.

For a given pigment, if a series of pigment-adhesive films of varying adhesive contents is formed, the specific volumes of the films (reciprocal of apparent density) may be used to examine their overall changes in structure. A series of pigment-adhesive films may be divided into two regions, the continuous or non-porous film region, where the adhesive volume is dominant, and the discontinuous or porous film region where the pigment forms a controlling skeleton.

In the continuous region, the volume of a pigment-adhesive film is determined by the sum of the pigment and adhesive volumes in the film. Mathematically, the continuous film region can be described by the equation:

$$V = V_p + V_a = v_p W_p + v_a W_a \qquad (1)$$

where

V = volume of the film, cc.,

V_p = volume of pigment, cc.,

V_a = volume of adhesive, cc.,

v_p = true specific volume of pigment, cc./g.,

v_a = true specific volume of adhesive, cc./g.,

W_p = weight of pigment in the film, g., and,

W_a = weight of adhesive in the film, g.

The specific volume of the film is:

$$v_f = \frac{V}{W} = \frac{V}{W_p + W_a} = v_p f_p + v_a f_a \qquad (2)$$

where f_p and f_a are the weight fractions of the pigment and adhesive, respectively. Since $f_p + f_a = 1$, Equation (2) may be written:

$$v_f = (v_p - v_a) f_p + v_a \qquad (3).$$

If the specific volume of a dry film is plotted versus the weight fraction of pigment, a straight line will be formed with an intercept of v_a when $f_p = 0$, and a slope numerically equal to $(v_p - v_a)$.

The discontinuous or porous film region, which is the region of interest in paper coating, may be described in the following manner. Let us assume that in the porous region there is insufficient binder to fill spaces between the packed pigment particles. The volume of the film is determined by the way in which the pigment packs, and the volume of the pigment. Further, let us assume that the pigment packs independently of the adhesive. Then the volume of the film is determined by the pigment according to the relationship:

$$V = X v_p W_p \qquad (4)$$

where X is a constant packing factor for the pigment. Dividing both sides of Equation (4) by W, the total weight of the film, we obtain:

$$v_f = Xv_p f_p \qquad (5).$$

In the porous film region, the specific volumes of the films should lie on a straight line of slope Xv_p passing through the origin. Figure 1 is a graphical representation of an idealized pigment-adhesive system which can be described by Equations (3) and (5).

The preceding assumptions used to describe a porous film system make this method suitable for testing the concept of idealized void filling or constant pigment packing. If packing of pigment independent of adhesive takes place, the linear relationship of Equation (5) will be valid and the specific volumes of films having $f_p > f_{p(C.P.V.C.)}$ will fall on the dotted line. Deviation from this relationship would show that something more than idealized void filling had taken place. If deviation occurs, the shape of the resulting curve should yield information on the type of changes that take place in film structure with changes in adhesive.

The particle orientations of selected films from a pigment-adhesive film series were determined to obtain a more complete picture of the contribution of the adhesive to pigment-adhesive film structures. Kraske (3) developed the technique for measuring the average particle orientation in a coating film. Murray and Johns (20) and Imamura and Yamaoka (21) have utilized this technique in connection with pigment coatings. If idealized void filling occurs, the average particle orientations of films within a series should not change with changes in the amount of adhesive present.

Finally, the changes in pore sizes with changes in adhesive content of a few selected films were examined by means of nitrogen gas adsorption. Some visual examinations of film pores by means of the electron microscope also were made.

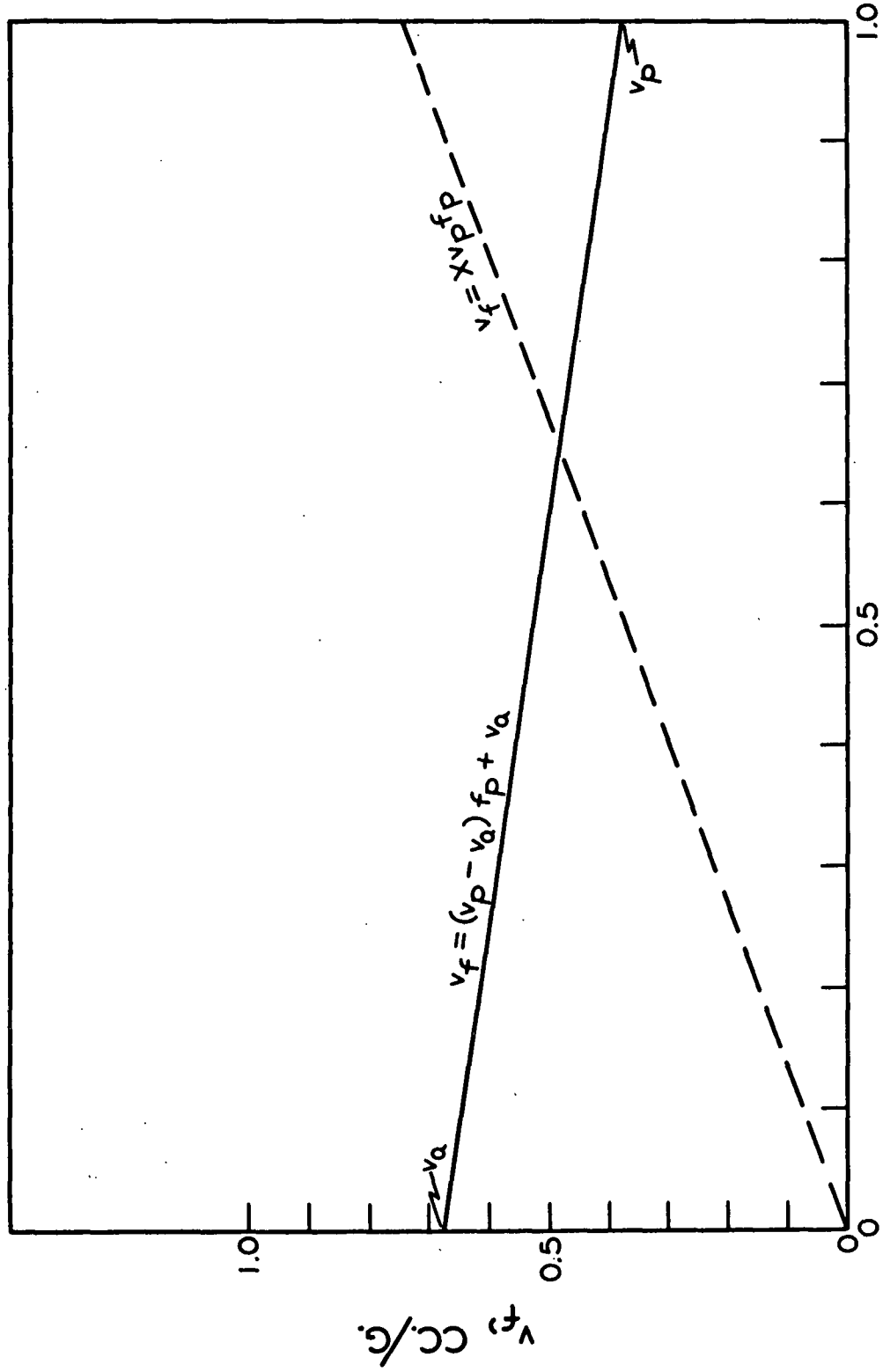


Figure 1. A Model System Representing Idealized Adhesive Void Filling

There are many factors besides the nature of the pigment and adhesive components which might affect the structure of pigment-adhesive films, and Kraske (3) has reviewed most of these factors in his study. Indirectly, such things as pigment dispersion and adhesive preparation might affect the arrangement of the components in a film. The substrate upon which a film is formed may have a pronounced influence upon the adhesive distribution in a film (22-26). All of the mechanical or process factors such as color preparation, film application, drying, and any further operations such as supercalendering may affect film structure.

EXPERIMENTAL PROCEDURES

In order to evaluate the role of the adhesive in the formation of pigment-adhesive film structures, all other factors which might affect film structure must be controlled. In this study the size and type of pigment and its dispersion were constant for all coating preparations. The vehicle used throughout the study was distilled water. All process factors involved in forming films such as preparing the coating color, applying the film, film drying, and film isolation were controlled. Also, the amount of pigment present in an applied wet film was kept approximately constant wherever feasible. Finally, the substrates upon which films were formed were such that the variable of substrate porosity was eliminated or accurately defined. The details of controlling the above factors are described along with the other techniques used in accomplishing the objectives of this thesis in the following discussion of experimental procedures.

SELECTION OF SUBSTRATES

All of the pigment-adhesive coating color systems studied were applied to tinfoil The tinfoil was obtained from the Matheson, Coleman, and Bell Company in 12 by 12-inch sheets having a thickness of 0.0005 in. The tinfoil represented a nonporous substrate from which the resulting coating films could be isolated readily. The foil eliminated the variable of substrate porosity, which may exert an influence on the role of an adhesive in structural formation.

Millipore filter HA was chosen as the porous substrate to which one of the coating color systems was applied. The average pore diameter of the filter is $0.45 \pm 0.02\ \mu$. The films formed from the same color system on both the porous and nonporous substrates were compared to indicate the effect of the substrate on structure. The films could be isolated readily from this substrate by dissolving away the filter paper.

PREPARATION OF COATING MATERIALS

PIGMENT PREPARATION

The pigment selected for this work was kaolin clay. A particle size of 0.5 to 1.0 μ equivalent spherical diameter (e.s.d.) was obtained by fractionating hydrous H.T. clay from the Minerals and Chemicals Philip Corporation. The fractionation was carried out using the sedimentation technique described by Holtzman (27) and later used on a large scale by Bergomi (28). The fractionation was begun with approximately 50 pounds of clay in a large stainless steel tank. After removing as much of the material of less than 0.5 μ e.s.d. as possible, several fractionation cuts were made to obtain a preponderance of particles between 0.5 and 1.0 μ. The dilute portions thus collected were centrifuged in a continuous manner on a Betafuge centrifuge to concentrate the suspensions. The thick pastes of each of the centrifuged separations were mixed together to assure a uniform supply of pigment throughout the thesis work. A total of approximately 18 pounds of slurry at 63% solids was collected. In order to facilitate color preparations, the clay slurry was concentrated further to 70% solids by means of filter candles.

The particle size distribution of the fractionated clay was checked by repeated fractionation in a basket-type centrifuge. Details of this procedure are given by Holtzman (27). The results are presented in Table I along with the results on similar clay materials used by Kraske and Bergomi for comparison.

The clay fraction prepared for this study was considered satisfactory. The percentage of the total particles obtained in the desired size range was greater than was prepared by other workers using similar techniques. This was due in part to a more complete removal of particles less than 0.5 μ e.s.d. It might be noted, however, that despite a great deal of effort, the complete elimination of

clay particles less than 0.5 μ e.s.d. was not particularly successful. This could have been due to the inefficiency of the process, or perhaps even to the creation of some smaller particles by the work necessary for dispersion between fractionation steps which may have caused further breaking up of clay particles.

TABLE I

CLAY PARTICLE SIZE DISTRIBUTION, % BY WEIGHT

	Particles < 0.5 μ	0.5 μ < Particles < 1.0 μ	Particles > 1.0 μ
This study	21	75	4
Kraske	29	69	2
Bergomi	40	30	30

The amount of dispersing agent (Quadrafos) required to give a minimum viscosity to the clay fraction was determined by measuring the Brookfield viscosity of 62.6% clay slurries. The pH of each test slurry was adjusted to 9.0 with 1.0N NaOH prior to the determination of its viscosity and the data are plotted in Fig. 2. The point of minimum viscosity was considered to represent maximum separation or repulsion of the individual particles. The graph indicates that 2-3 milliequivalents of Quadrafos for each 100 g. of clay were required to disperse the clay slip to its minimum viscosity at this pH level.

ADHESIVE SELECTION

The adhesives selected for study were a starch, a polyvinyl alcohol (PVA), and a latex. The starch represents a colloidal adhesive system, the PVA a solution system, and the latex an emulsion system. These adhesives were selected so that the hypothesis of the idealized filling of voids by an adhesive could be evaluated for three widely differing adhesive systems. Also, of course, comparison of the three systems will determine whether or not the adhesives differ with regard to the formation of pigment-adhesive films.

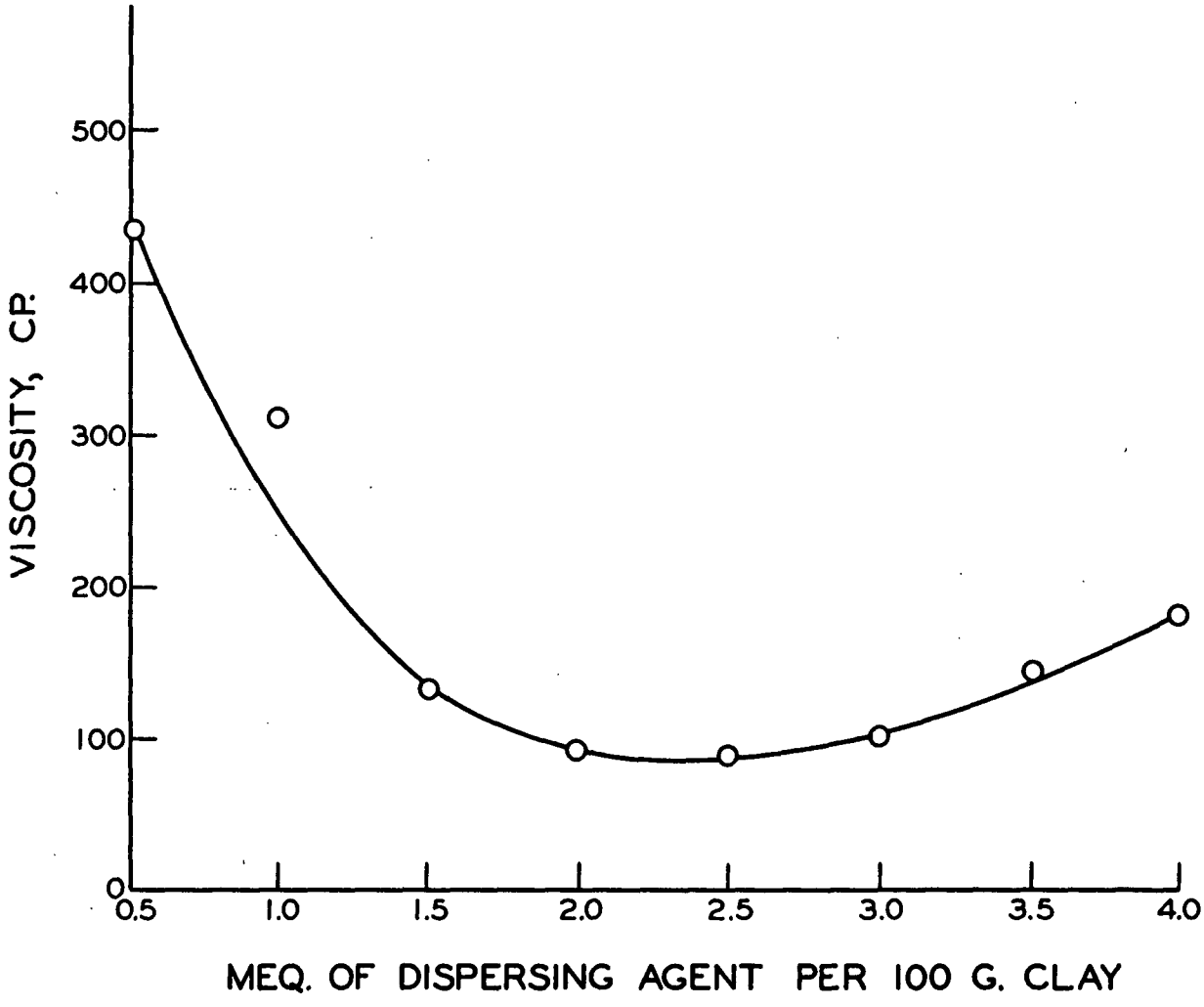


Figure 2. Dispersing Agent Requirement for Prepared Clay Fraction

The starch used was a dextrinized starch (Clinton 632) manufactured by the Clinton Corn Processing Company. This starch was selected over oxidized coating starches used in previous studies (3,4) because it gave a smooth, pit-free surface in a pigment-adhesive film. Work by Bergomi (28) and Garey (29) indicated that pitted coatings are formed when oxidized starches are used as binders, and this observation was confirmed in the present study. Since surface aberrations interfere with the density determinations necessary in this study, the dextrinized starch was more suitable. A dextrinized starch is a starch which has been modified by acid hydrolysis and dry heat (30,31). The result is a compact, highly branched starch molecule. The viscosity and pigment-adhesive film strength characteristics of the Clinton 632 were found to be satisfactory for the present work.

The polyvinyl alcohol selected was Du Pont's Elvanol 71-30. This is a fully hydrolyzed, medium-range molecular weight material that is generally recommended as a pigment coating binder.

The latex selected was a styrene-butadiene copolymer marketed by the Dow Chemical Company as Dow 512-R. This latex has a styrene-to-butadiene ratio of 60/40 and an average particle size of 0.2 μ. Dow 512-R is stabilized principally with a nonionic system.

The starch was cooked at 35% solids in accordance with the method (32) used for preparing starch in the Corn Industries Viscometer (C.I.V.). The polyvinyl alcohol was prepared by cooking at 10 to 15% solids also in the C.I.V. using a procedure similar to that recommended for preparation of the starch. The latex was used directly in the coating colors as received from the manufacturer.

PREPARATION OF COATING COLORS

All of the coating colors were prepared in the following general manner. A slurry of the clay fraction was prepared at 67% solids using 2.5 meq. of

Quadrafos and 3.0 meq. of NaOH per 100 g. of clay by mixing for 30 minutes with a Hamilton-Beach stirrer. The required amount of clay (at 67% solids) was mixed with the required amount of prepared adhesive to give a final color of the desired adhesive-to-pigment ratio. The pH of the color was adjusted to 9.0 with 1.0N NaOH, sufficient water was added to give the specified solids content, and the color was agitated for 30 minutes with a Hamilton-Beach stirrer. The colors were made up in 50-g. total weight batches and then screened through a 325-mesh sieve. Each color was deaerated for 15 minutes with a water aspirator. Throughout this deaeration, the color was agitated with a magnetic stirrer. In a very few instances, a color resisted deaeration and was quite foamy, and in these cases the color was subjected to 5 minutes' deaeration with a Hi-Vac vacuum pump.

COATING APPLICATION

The coating colors were spread on the tinfoil and Millipore filter with Bird applicator bars. The volume of wet color per area of substrate (and thus the volume of pigment per area) could be controlled approximately by using bars of different clearances or by shimming a given bar. The pigment quantity applied per area of substrate was kept essentially constant for most films by varying the wet film applied and the color solids. Certain films of high adhesive content required that less pigment be present.

In order to spread the colors on tinfoil, the following technique was developed. The glass surface upon which the foil substrate was laid was moistened with water. The foil was then pressed flat against the moistened surface and taped in place with cellophane tape on all four sides. This procedure assured that the substrate would lie flat during application and drying of a film. This flat surface was important so that wrinkling of the foil during drying would not occur and cause flow of the wet film and formation of an uneven final film. A puddle of coating color was then placed on the foil and spread with the applicator bar.

The technique for fastening the Millipore filter, forming a color pond, and then spreading this pond with a Bird applicator bar to give a film was the same as that described by Kraske (3).

DRYING

All films were air dried at 73°F. and 50% R.H. These are mild drying conditions.

ISOLATION OF COATING SAMPLES

It was necessary to isolate the coating films from their respective substrates to accomplish the objectives of this study. The presence of a substrate seriously complicates, and sometimes prevents, the analysis of coating structure. The substrates used in this study were selected because they could be separated easily from the coating films.

Coating films formed on tinfoil substrates were isolated by dissolving away the foil in mercury. Samples were placed, foil side down, on pools of mercury held in culture dishes which were found to be suitable reservoirs for the mercury. After a period of time, the samples could be removed from the surface of the mercury and the substrate side of the films brushed with a small brush to remove any remaining material. Three contacts with fresh mercury followed by light brushing were sufficient for complete removal of the foil. Nearly all of the foil is removed in the first contact with mercury. The other two cleanings remove any small traces which might remain.

The isolation of coating film samples from Millipore filter by dissolving the filter paper in ethyl acetate was identical to the procedure described by Kraske (3). After substrate removal, the isolated coating films were air dried on pieces of Teflon tape.

PHYSICAL DETERMINATIONS

FILM DENSITIES

The most important physical determination to be made was the determination of the density of a coating film. The literature is full of methods to determine the actual density of porous materials. However, here we are interested in the apparent density, or the weight of material per total film volume (volume of pigment + volume of adhesive + internal void volume). Some elaborate techniques are described in the literature for determining apparent density (33,34). These techniques, despite the time and equipment involved in utilizing them, do not seem to give exceptionally good reproducibility of results.

Kraske (3) and Eames (4) used a mercury pycnometer to determine coating film densities, but this specific technique was found to be unsatisfactory in the present work. The technique of determining film densities by weighing in mercury and in air as suggested by Pierce and Holsworth (19) and Cole (18) was also considered. Both of these general techniques have severe limitations due to the properties of the films and also problems inherent in the procedures. The films under study were only about 30-40 μ thick, and ranged from 0 to 100% adhesive, based on the weight of pigment. The films of low adhesive content were extremely weak or fragile and could not be immersed in the mercury without breaking. The mounting of such fragile samples for attempted immersion is in itself a problem.

The samples in such mercury techniques were to be mounted or held so that they could be surrounded with or submerged in the mercury. The samples displaced such a small volume of this liquid that any holder which excluded the mercury, for instance by inaccessible spaces between clamps and the sample, seriously affected the results. In the case of the pycnometer, samples were forced against the sides of the pycnometer, and certain areas became inaccessible.

Aside from techniques utilizing mercury, the most common method of determining apparent density is by direct weight and volume measurements on a film. The limiting factor here appears to be an accurate measurement of film thicknesses. Pierce and Holsworth (19) describe a method of measuring film thicknesses using a micrometer. This technique is good, at best, to 0.0001 in. or 2.54 μ, and is subject to error caused by gross surface irregularities. Pellett (35) describes a technique for measuring film thicknesses based upon the area assumed by a drop of liquid of known volume placed in a cavity scraped in a coating film. This method has experimental drawbacks.

The method finally developed for measuring film densities or specific volumes is based upon the direct measurement of weight and volume and is described in the section that follows.

Samples were cut from a coating film, as shown in Fig. 3, and the substrate was then removed from the film samples. Section A of Fig. 3 was designated as the weight-per-unit-area sample, and Sections B and C were designated as thickness samples. The weight/area sample was photographed with a Polaroid-Land camera using an optical system such that a photograph of approximately 3X magnification was obtained with Polaroid positive-negative film. The positive was planimetered five times and the average used to determine the exact surface area of the sample. The exact magnification of the positive was obtained by placing a scale over the sample and then using the negative of the Polaroid film to measure the magnified scale on a microcomparator. The exact magnification was found to be 3.1625X. Obviously, knowing the magnification of the photograph and the planimeter constant, the X-Y planar area of the sample could be determined. After photographing, the weight/area sample was oven dried at 100°C. and weighed

on a semimicrobalance to determine the weight of the given area of the sample. The sample was then ashed for 3 hours at 915°C. After cooling, it was reweighed and the amount of pigment was determined from the ash, and the adhesive present was found by difference.

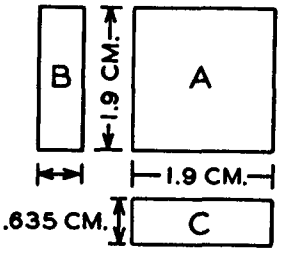


Figure 3. Cutting of a Film Sample for a Density Determination

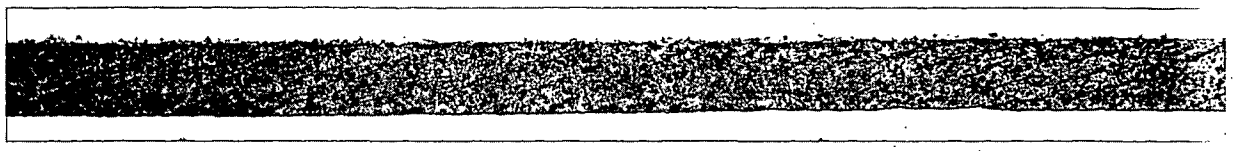
The thickness samples, Sections B and C, were placed in gelatin capsules and then mounted in butyl methacrylate. The samples were microtomed or cross sectioned along their sides which adjoined the periphery of the weight/area sample. These cross sections were mounted on slides and were photographed at two spots along their length at approximately 300X. Thus, four thickness estimates for each weight/area sample were available. The exact magnification at which the cross sections were photographed was again determined by photographing a scale and measuring its resulting magnification on a microcomparator. The magnification was determined to be 300.20X. The negatives of each of the four rectangular thickness cross sections were planimetered five times and the average value used to obtain average thickness. Knowing the magnification of the negative, the planimeter constant, and the length of the cross section, the average thickness could be calculated, and the average of the four sections represented the average thickness for the weight/area sample.

When determining the thicknesses of latex-clay films, the samples to be cross sectioned were not mounted in butyl methacrylate. Instead, they were merely covered with a very thin film of collodion, placed between two glass microscope

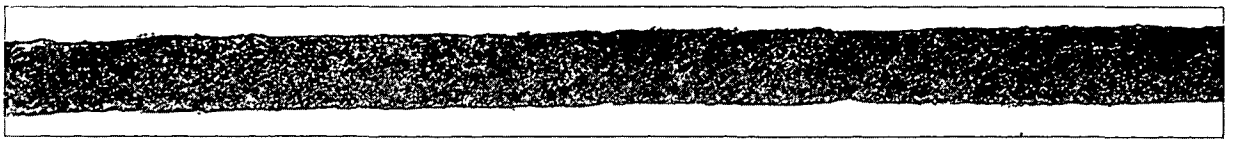
slides for support, and then sectioned. This method of supporting latex-clay samples for sectioning was used to avoid any possible attack of the butyl methacrylate upon the latex binder. Examples of typical coating film cross sections are shown in Fig. 4.

Dividing the weight/area of a film by its thickness yields the density of the film. In a density determination such as the one described, it is very important that the film be uniform in thickness, at least throughout a given weight/area section. This uniformity in film thickness was determined by taking a representative weight/area section and evaluating its thickness by the method just described at various points over its surface. Uniformity in thickness throughout a weight/area sample was reflected also in the reproducibility of the density determinations. A reported density must be reproducible anywhere within a given coating film, and coating films from the same coating color must have the same density. The reproducibility of a film density determination within a film and between films from the same color was found to be highly satisfactory, as shown by the reproducibility data presented in Appendix I, Table III.

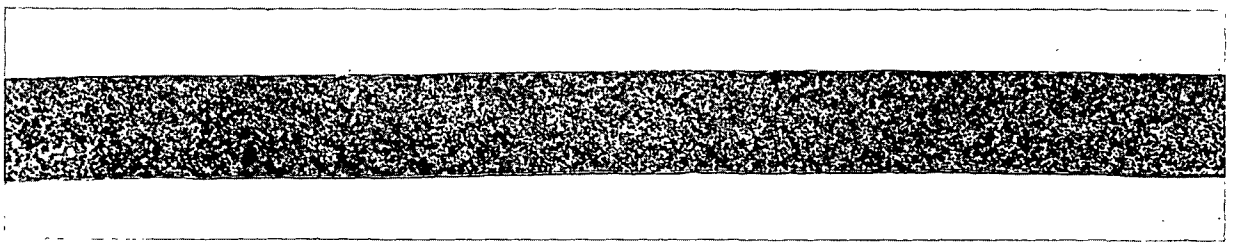
The possibility of an error in the determination of film thickness caused by a compaction of thickness specimens due to a shrinkage of the butyl methacrylate mounting material was checked. A piece of coating sample was broken in half and one half was mounted in butyl methacrylate while the other half was mounted in an epoxy material (Epon 812) which exhibits much less shrinkage than the butyl methacrylate upon drying. Examination of cross sections taken along the common edge between the pieces of the coating sample in each of the mounting materials gave the same value for the film thickness. Thus, it was concluded that the shrinkage of butyl methacrylate did not affect thickness determinations.



(a) PVA-Clay Film (300X) Formed on a Nonporous Substrate



(b) PVA-Clay Film (300X) Formed on a Nonporous Substrate; From the Same Coating Film as (a) Above



(c) Latex-Clay Film (300X) Formed on a Nonporous Substrate

Figure 4. Typical Coating Film Cross Sections

A slight modification of the preceding film density technique was necessary for determining the density of a 100% pigment film. Samples of the pure pigment films had to be peeled from the foil and Millipore substrates. The pieces were irregular, and the thickness samples did not always correspond exactly to the periphery of the weight/area sample. Aside from the isolation and the extreme care needed in handling samples, the usual procedure for determining densities was followed.

ADHESIVE FILM DENSITIES

The densities of films of the Clinton 632 starch and polyvinyl alcohol were determined using a density gradient column technique similar to that described by Boyer and Spencer (36) and Osta and Yamamoto (37). The gradient was a benzene-carbon tetrachloride column calibrated with zinc chloride solutions. The calibration curve and data for the adhesive film densities are given in Appendix I. The density of the starch film was also determined by the method developed in this study for determining the densities of the pigment-adhesive coating films. The gradient column and coating film technique showed good agreement (see Appendix I).

Because of difficulties in establishing an inorganic column of the proper density range, the density of a latex film was determined by a simple flotation method. Sodium hydroxide solution (30%) and distilled water were mixed until a sample of the latex film just floated upon the surface. The density of the liquid upon which the sample would float was determined pycnometrically, and an average from three determinations was used as the density of the latex film.

MEASUREMENT OF THE AVERAGE CLAY PARTICLE ORIENTATIONS OF COATING FILMS

The measurement of the average clay particle orientations of coating films was by the method of Field and Merchant (38) as adapted by Kraske (3) for thin films. Imamura and Yamaoka (21) and Bundy, Johns, and Murray (39) also have used this technique to study clay particle orientations in paper coatings. Kraske (3) has thoroughly discussed the principle behind the method and the experimental procedures involved. Only a brief description of the principle and any refinements of the technique which have been made will be given here.

A kaolin crystal is so constructed that the (001) crystal plane is parallel to the large surface of the clay particle. Any regularly, minutely spaced planes are capable of diffracting an x-ray beam incident upon them at certain angles. The angle at which diffraction occurs is related to the spacing of the crystal planes through Bragg's law (40). The intensity of the diffracted x-ray beam is proportional to the mass of material properly oriented for diffraction. If an x-ray source and a diffracted beam are held in the correct position for diffraction from a given crystal plane, and the sample is rotated about an axis perpendicular to the plane of the x-ray beams to an angle, α, the intensity of the diffracted beam, measured under these conditions, is due to the number of crystal planes oriented at the angle α to the surface of the specimen. For a clay coating, the diffraction intensity is proportional to the number of crystal planes in the clay platelets which in turn are oriented at a specific α to the sample surface. By examining the diffracted x-ray intensity of a given coating at a number of different α's, a relative estimate of the degree of orientation of the clay in the coating can be made. When a plot is made of the relative intensity of the diffracted beam *versus* the angle of tilt, α, the slope of the function obtained which appears linear over the angular range studied is the numerical estimate of the degree of

orientation. The greater the numerical value of the slope, the higher the clay platelet orientation parallel to the substrate upon which the coating was formed. A perfectly random particle orientation would have a 0.0 slope.

In a method of measuring orientation such as the one described, a correction must be made for differences in adsorption of the diffracted beam caused by changes in path length. The measured intensities at various values of α can then be compared with one another and with the value obtained at $\alpha = 0$. The relative intensity of the diffracted beam is the intensity at a particular α compared to the intensity $\alpha = 0$. Also, a correction is needed to compensate for the fact that coating samples are not infinitely thick to x-rays. The derivations for the calculation of relative intensities and for the two correction factors as developed by Field and Merchant (38) and Kraske (3) are presented in Appendix I. Information concerning the reproducibility of the technique is also presented.

Within a series of pigment-adhesive films, the comparison of particle orientation values gives an estimate of the relative degree of clay platelet orientation among films in the series. Thus, if no changes in the clay platelet packing take place within a film series with increasing amounts of adhesive, the particle orientation of all films should be identical. Differences in measurable orientation among films show that changes in the pigment packing are occurring.

The x-ray technique used in this study differed from that of Kraske in a few minor ways. A new linear proportional counter was used on the x-ray unit which permitted direct comparison of peak intensities within a sample. An older Geiger counter was in use at the time of Kraske's work. Film thickness measurements were known exactly in the present study, while Kraske relied on thickness values calculated from questionable density determinations. Finally, adsorption coefficients of coating films were determined in this study from actual experimental

film densities. Kraske determined adsorption coefficients by using densities calculated from a summation of the solid components. However, a comparison of orientation results using coefficients based on experimental densities and calculated densities showed negligible differences. Composite samples of four pieces of film from a given coating, as recommended by Kraske, were used in this study to obtain an average orientation for a coating film.

DETERMINATION OF SURFACE AREAS AND PORE DISTRIBUTIONS OF COATING FILMS

Nitrogen gas adsorption was used to determine surface areas and pore distributions of a limited number of coating films. Haselton (41) has presented a review of various gas adsorption methods. The method used in this study to obtain coating film surface areas was that of Brunauer, Emmett, and Teller (42). These authors have developed expressions based on a multilayer gas-adsorption theory which may be used to describe most adsorption isotherms over a wide range of relative pressures. The Brunauer, Emmett, and Teller (B.E.T.) equation for the isothermal adsorption of molecular layers of a gas may be used in the low relative pressure range to calculate the surface areas of coating films. The equation is presented in Appendix I. The use of the B.E.T. method and the necessary equipment and its operation are discussed in detail by Haselton (41), and by Merchant (43), and in the Institute gas adsorption procedures (44). Further discussion of the techniques involved in determining surface areas would be repetitive.

Kraske (3) has presented a complete discussion of the determination of pore size distribution and void volumes of coating films by nitrogen gas adsorption. Pore distribution determinations are based upon the interpretation of the adsorption-desorption isotherms obtained with low-temperature gas adsorption techniques (45). Pierce's (46) interpretation of the desorption portion of an isotherm,

which is based upon the assumption of the validity of the Kelvin equation over the range of pore sizes in question, was used in this study. Kraske (3) showed that Pierce's treatment was applicable to some coating films. For the coating films considered in this study, the method of determining pore distributions by gas adsorption has only limited applicability. The reasons for this limited usefulness will be discussed with the results of the gas adsorption work.

The Kelvin equation and Pierce's assumptions which make it suitable for interpretation of the desorption portion of an isotherm to describe pore distributions are presented in Appendix I. The equipment and procedures necessary for determining pore distributions are, again, those of Haselton (41) and Merchant (43).

ELECTRON MICROSCOPY WORK ON COATING CROSS SECTIONS

In the course of examining the results obtained in this study, some unusual indications regarding the pore sizes of coating films came to light. A visual confirmation of these results by means of the electron microscope was of great value. Electron micrographs of the surface of clay-coated papers have been made (47-49). Some attempts have been made to estimate pore sizes by electron microscopy (50,51) as a check on gas adsorption work. However, no meaningful coating cross-section electron micrographs actually have been published. To visually estimate coating pore sizes, an electron micrograph of a cross section is necessary. In this study, it was possible to take an isolated coating film thickness sample (see film density technique), mount it in a suitable material, and cut ultrathin sections that could be examined with the electron microscope. In some cases, Maraglass proved to be a more suitable material for mounting samples for examination with an electron microscope than was the butyl methacrylate which had been used in the density procedure discussed previously. The sectioning and photographing was done by the technique of Smith (49), and the work was carried out in her laboratory.

PRESENTATION AND DISCUSSION OF THE EXPERIMENTAL RESULTS

It will be helpful to keep in mind throughout the following discussion that the three main objectives of the study are: (1) to determine what a specific adhesive is doing — exhibiting idealized void filling, or combining in a more complex manner; (2) to determine if adhesives differ with respect to the manner in which they combine with a given pigment during film formation; and (3) to determine the effect of the substrate upon the arrangement of the pigment and adhesive within a coating film.

PIGMENT-ADHESIVE FILM SYSTEMS ON A NONPOROUS SUBSTRATE

Films from the three different pigment-adhesive coating color systems were formed by applying the colors to a nonporous substrate. Here the role of the adhesive in film structural development can be evaluated without the complicating variable of substrate porosity.

Before discussing the relationship between a clay pigment and an adhesive in film structures, it is helpful to visualize how these materials may be brought together to establish a film structure. A coating color is applied to a substrate, usually by a roll or blade process. The shearing forces created in the color by the coating process may tend to align some of the platelike clay particles parallel to the substrate in the resulting wet film. Immediately after the application of the wet coating film to a nonporous substrate vehicle evaporation begins. This evaporation takes place at the air-film interface. As evaporation continues, the thickness of the wet film decreases in a direction normal to the substrate (the z-direction). As the thickness decreases, the pigment particles in the wet film are brought closer and closer together. At the same time, the concentration of the adhesive present in the liquid phase is increasing.

Finally, enough evaporation has taken place so that the pigment particles begin to contact one another, or are separated by associated adhesive material and perhaps small amounts of concentrated adhesive solution. When this stage is reached, the pigment particles are probably immobilized, or certainly greatly hindered from further movement. From this point on, a definite skeleton or pore structure begins to become established. Evaporation continues at the film surface as long as the pore or capillary system established is capable of supplying liquid. The vehicle or evaporation interface gradually recedes into the coating as the supply rate diminishes. Then menisci begin to form in the capillary skeleton of the coating. When these menisci form, surface tension forces similar to those discussed by Campbell (52) for fibers and by Haines (53) for solid spherical particles are exerted on the structure. As the vehicle menisci retreat further, the contracting forces of the menisci are replaced partially by the final adhesive bonds which hold the pigment particles together. The end result is a rigid, porous, pigment-adhesive structure.

A. STARCH-CLAY FILM SYSTEM

The first coating film system to be considered is a starch-clay system on a nonporous substrate. The specific volume determinations on starch, clay, and starch-clay films are shown in Fig. 5 in the manner described previously for evaluating an idealized void-filling model. The tabulated data from which Fig. 5 was prepared are given in Appendix II, Table VII.

The experimental value obtained for the specific volume of the starch used was 0.674 cc./g., while that for the clay was 0.385 cc./g. The straight line in Fig. 5 connecting the specific volumes of the starch and clay describes the weighted sum of the specific volumes of the two materials at any starch-to-clay ratio. Any experimental points that fall on this line represent the specific volumes of continuous or nonporous films.

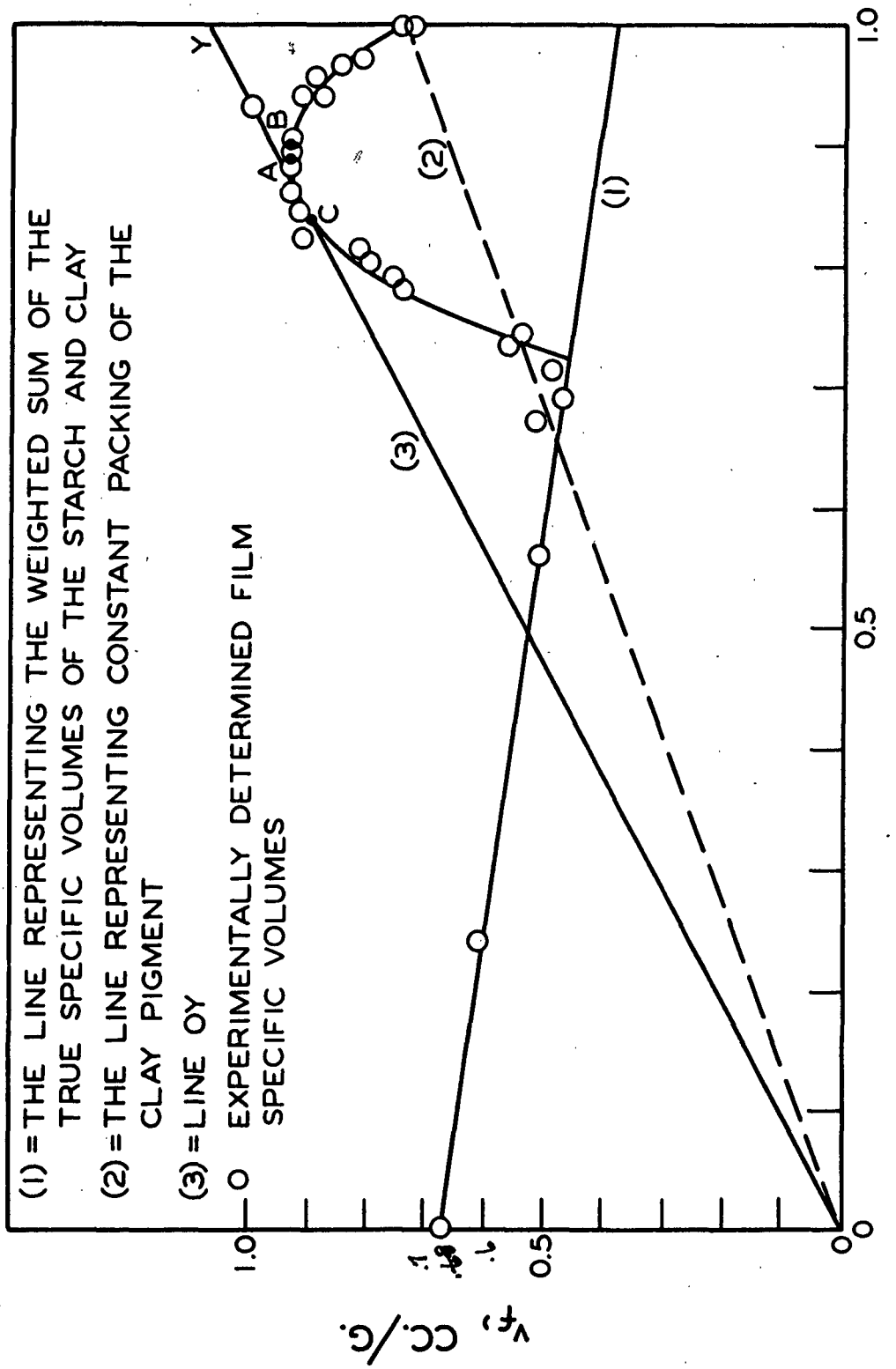


Figure 5. Effect of Changes in Weight Fraction of Pigment, $f_{\underline{p}}$, on Film Specific Volume, $v_{\underline{f}}$, of Starch-Clay Films

The specific volume of a film of clay pigment alone formed on a nonporous substrate was determined to be 0.74 cc./g. The difference between this value and that obtained for the solid clay (0.385 cc./g.) is equal to the void volume of the pigment film. The dotted straight line joining the specific volume of the pigment film and the origin ($v_f = 0$, $f_p = 0$) in Fig. 5 represents constant packing of the clay pigment in a film in a manner independent of any starch present. That portion of the dotted line which extends from the specific volume of the 100% pigment film to its point of intersection with the line representing the specific volumes of continuous starch-clay films represents idealized void filling in the porous starch-clay film range. The point of intersection of the two lines is the critical pigment volume concentration for the idealized system (see page 7 of this thesis) and has a value of 0.480 cc./g. at a weight fraction pigment of 0.645.

The specific volume of 0.74 cc./g. for the pigment film is believed to be a reliable datum point within a small range of experimental error. The difficulties involved in the determination of the specific volume of a clay pigment film were pointed out in the discussion of the experimental procedures. The value of 0.74 cc./g. is in good agreement with what would have been obtained by extrapolating the starch-clay film specific volume values in Fig. 5 to $f_p = 1.0$. This value obtained for the specific volume of the pigment film also corresponded quite well to values that may be calculated from Hagemeyer's data on the relative sediment volumes for the packing of kaolin particles (10). Hagemeyer's relative sediment volumes correspond to specific volumes of 0.70 to 0.76 cc./g. when converted for comparison.

The data points obtained in this study for the specific volumes of starch-clay films in the porous film region do not fall on the dotted straight line in Fig. 5, as required by the simplifying hypothesis of idealized void filling. These experimental values show that the film specific volume increased with initial

increments of starch. This increase in specific volume continued until a maximum was reached. The maximum specific volume represented by Point A in Fig. 5 is shown at a weight fraction pigment of 0.89 to 0.88 (12-14 parts starch/100 parts clay), and was determined to be about 0.94 cc./g. as compared to 0.74 cc./g. for the clay pigment film.

An examination of Fig. 5 reveals that the internal void volumes of the starch-clay films must have changed with the quantity of starch present. The void volumes of films, cc./g., at a given weight fraction of pigment, are represented by the vertical distances between the experimental specific volume curve and the continuous film line. The continuous film line represents not only the weighted sum of the specific volumes of the film components, but also the sum of the volumes of the starch and clay components on a gram total weight basis (see derivation on page 11 of this thesis). The internal void volumes of the films increased with initial amounts of starch and passed through a maximum value. The maximum void volume occurred at the point at which the tangent to the experimental specific volume curve was parallel to the continuous film line. This point is designated at Point B in Fig. 5. For clarity, the void volume data at chosen points along the experimental curve in Fig. 5 were replotted as void volume per gram of film, cc./g., versus film weight fraction pigment, as shown in Fig. 6. The maximum point in the curve in Fig. 6 corresponds, of course, to Point B in Fig. 5. The maximum void volume was found at $f_p = 0.90$, which was at a slightly lower starch content than the point of maximum film specific volume.

It is apparent that for films to exhibit either an increased specific volume or an increased pore volume with initial increments of starch, an expansion of the pigment skeleton must have taken place. Referring again to Fig. 5, if a line is projected from the origin ($v_f = 0$, $f_p = 0$) through a point on the experimental specific volume curve to the specific volume axis at $f_p = 1.0$, then the

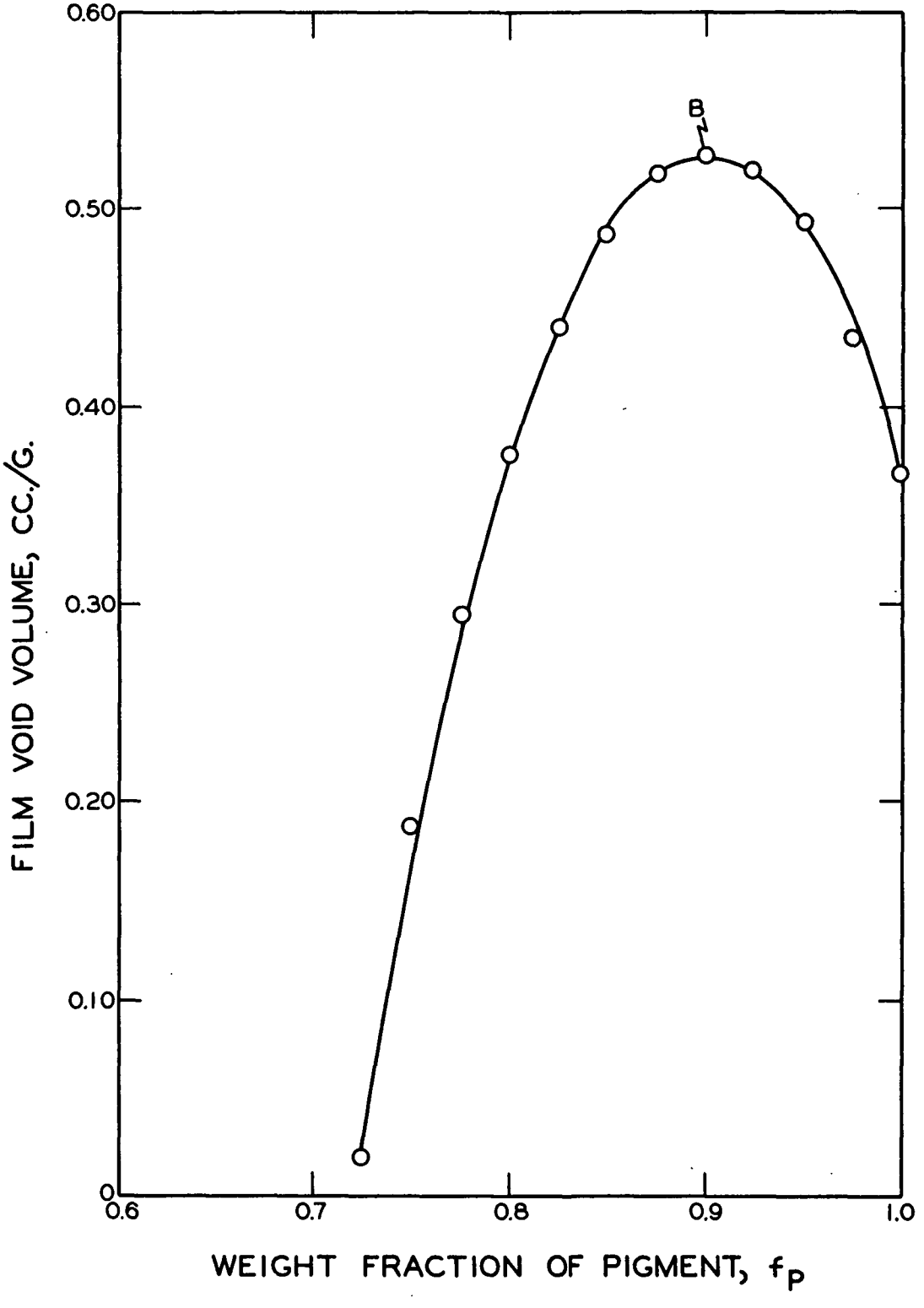


Figure 6. Changes in Film Void Volume with Changes in Weight Fraction of Pigment, f_p, for Starch-Clay Films

intercept of the line at $f_{-p} = 1.0$ represents the specific volume of a pigment film which would be obtained simply by removing the binder from within the pigment skeleton of that particular film on the experimental curve without disturbing the arrangement or packing of the pigment particles in the skeleton. The higher the intercept at $f_{-p} = 1.0$ of a line drawn as described, the more expanded the pigment skeleton must be. If a family of lines is drawn from the origin through points on the experimental curve, the projected intercepts or specific volume values for corresponding pigment films increase and go through a maximum. The maximum intercept of a line at $f_{-p} = 1.0$ occurred with line OY in Fig. 5. This line is a line tangent to the curve defined by the experimental specific volume values at about $f_{-p} = 0.85$ to 0.84 (18-19 parts starch/100 parts clay). This point of tangency, designated as Point C in Fig. 5, represents the starch level at which the most expanded pigment skeleton occurred. This maximum film expansion occurred at a higher starch level than that at which the film specific volume or void volume showed a maximum.

The relationship of Point B, maximum film void volume, to Point C, maximum film expansion, is shown more clearly by replotting selected experimental points from the specific volume curve obtained in Fig. 5 as film volume per gram of pigment versus the volume of starch per gram of pigment, as in Fig. 7. This method of presenting the data also has the advantage of allowing estimates of the rate of change in the pigment skeleton with increasing amounts of starch. On such a plot, the idealized void-filling model would follow the dotted horizontal line until a continuous film was reached, and would then extend upward with a slope of 1.0 as added increments of binder caused equal increments of increase in the volume of film containing 1 gram of pigment.

The rate of change in film volume per gram of pigment with the change in starch volume per gram of pigment is merely the slope of the curve in Fig. 7 at

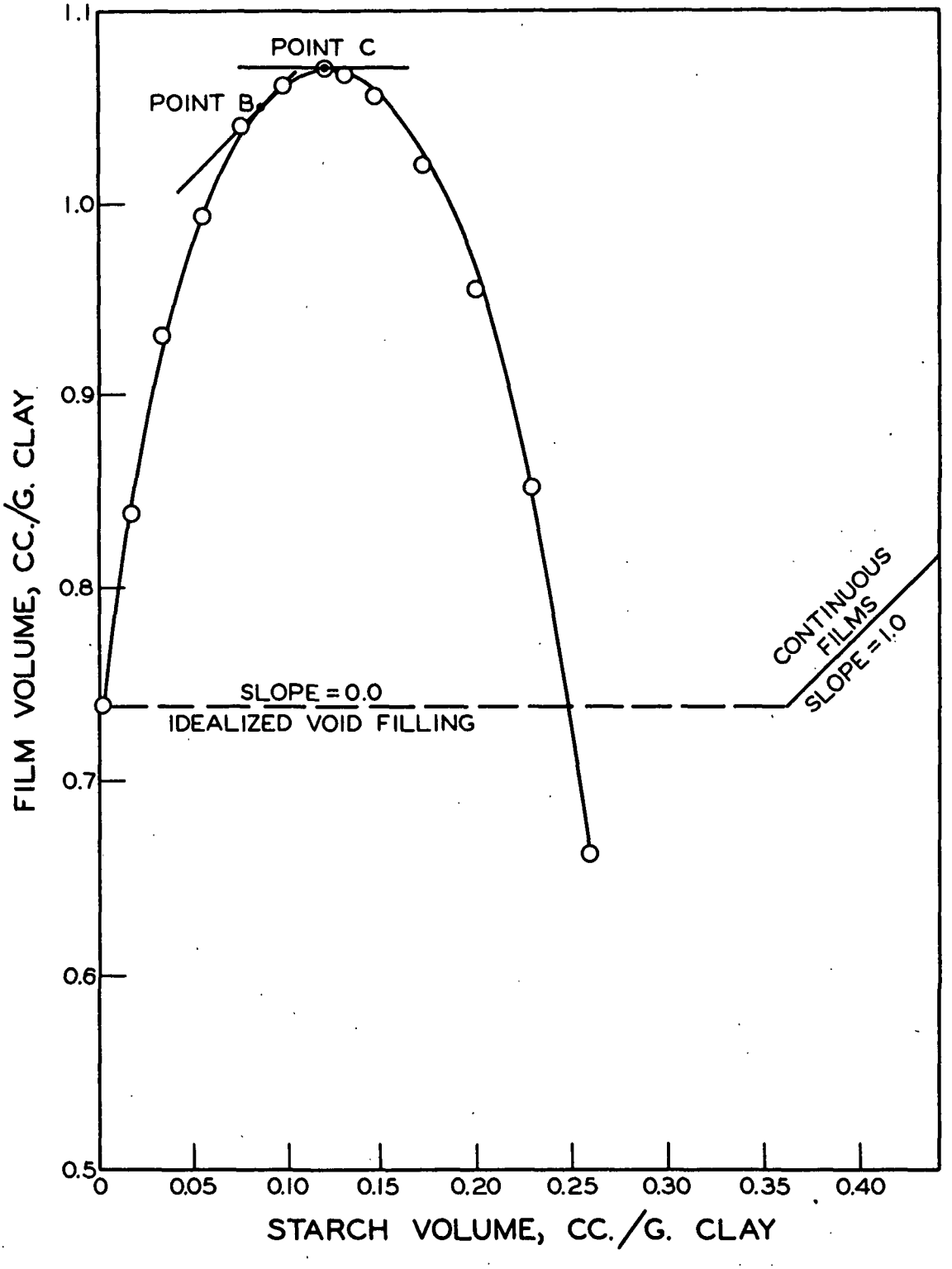


Figure 7. Changes in Film Volume per Gram of Clay with Changes in Starch Volume per Gram of Clay for Starch-Clay Films

any point. Where the slope of the curve is greater than 1.0, film volume was increased by more than just the additional volume of starch. The pigment skeleton was expanded to the extent that an increase in void volume occurred. Where the slope equaled 1.0, the increase in film volume was equal to the volume of starch added. Here the pigment skeleton expanded, but the internal void volume remained constant. The point on the curve in Fig. 7 where the larger initial slope decreased to 1.0 thus represents maximum film void volume and corresponds to Point B on Fig. 5. A positive slope of less than 1.0 indicates that film volume was increasing, but by less than the volume of added starch. Here the pigment skeleton was expanded, but the void volume was decreased by the additional starch. The peak in Fig. 7 represents the maximum film volume obtained by increases in volumes of starch, and thus the maximum expansion of the pigment skeleton of the film. This peak corresponds to Point C on Fig. 5.

A negative slope, of course, means that the film volume was decreased as the volume of starch was increased. For the film volume to decrease with increasing volumes of starch, the pigment skeleton must have undergone a compaction, and the pigment particles packed in such a manner as to reduce the space between the particles.

It should be emphasized that if over any segment of the experimental curve in Fig. 7 the slope of the curve had been equal to 0.0, idealized void filling would have occurred between the starch-clay films which were connected by the segment. However, over no segment of the experimental curve in Fig. 7 was the slope equal to 0.0, and thus no porous starch-clay film was formed by the addition of starch in an idealized void-filling manner to a preceding film of greater weight fraction of pigment. This conclusion may also be stated by saying that if even an infinitesimally small increase in the starch content of a film was made, this increase was accompanied by an alteration in the pigment matrix of the film.

After the point of maximum film expansion (Point C in Fig. 5 and the peak in Fig. 7), the starch-clay films densified rapidly due to the compaction of the pigment skeleton which caused a reduction in the interpigment void space to be filled by the starch. Films just prior to the continuous region actually had greater densities or lower specific volumes than could ever be obtained by an idealized filling of voids in the pigment film. This is illustrated in Fig. 5 where the experimental curve crosses and drops below the dotted line representing idealized void filling. A continuous film, and thus the critical pigment volume concentration of the system, was obtained at $f_p = 0.725$, as compared to a value predicted by idealized void filling at $f_p = 0.645$. When the starch content reached this level, the pigment particles were compacted more closely than in a film containing clay pigment alone. When the continuous film region was reached, the behavior of films was as predicted. Experimental values in this region fall on the theoretical line which represents the weighted sum of the specific volumes of the starch and clay.

Gas Adsorption Studies on the Starch-Clay Film System

It was shown that the void volumes of the starch-clay films studied changed with increasing amounts of starch due to expansion and then compaction of the film pigment skeleton as well as to the filling of voids by starch. These changes in void volumes among films were studied by means of gas adsorption techniques to help explain the nature of the changes in pore sizes which accompanied the changes in total film pore volumes, and thereby better describe the changes in starch-clay film structures caused by variations in the starch content of films.

Four significant films were chosen for study. The samples selected included a film from the region of increasing void volume, a sample at approximately the maximum film void volume, a sample just at the beginning of the films of decreasing void volume, and a final sample from the region of rapidly decreasing film void volume.

The surface areas of the four coating samples, as determined by gas adsorption, and their total pore volumes, as calculated from the specific volume determinations, are presented in Table II.

TABLE II

SURFACE AREA MEASUREMENTS ON STARCH-CLAY FILM SAMPLES

Sample Number	Sample Designation, f_p	Surface Area, $m.^2/g.$	Total Pore Volume, cc./g.
1	0.9565	6.41	0.468
2	0.9058	4.76	0.525
3	0.8572	3.38	0.497
4	0.8036	2.26	0.380

The data in Table II show a continual decrease in the surface areas of the films with increasing starch content. However, there was an increase in film pore volume between the first two samples. This indicates that a shift in the pore size distributions toward larger pores occurred between these two films. The net effect of more large pores and fewer small pores would explain the experimentally observed increasing void volume with decreasing surface area. Blumental, Sourirajan, and Nobe (54) have shown the marked effect of pore size change on surface area. In their work a sample with an average pore radius of 37 A. had a surface area of 272 $m.^2/g.$ A sample of the same material with an average pore radius of 3100 A. and of approximately the same void volume, had a surface area of only 1.3 $m.^2/g.$ Kraske (3) showed that shifts in pore sizes in coating films can yield increases in void volumes while surface areas decrease.

The last two film samples in Table II had both decreasing surface areas and void volumes with increasing starch content. The sample just after the beginning of decreasing void volumes (f_p = 0.857) had a reduced surface area due largely to

the reduction in void volume by the filling of voids because at this point the pigment skeleton was still expanding. The final film sample had decreased surface area both because of the filling of voids and because of the reduction in void volume resulting from the compaction of the pigment skeleton of the film. The changes in size of the pores in these last two samples cannot be determined from surface area and total pore volume data.

It was hoped that nitrogen gas adsorption could be used to determine both the pore size distributions and the total pore volumes in the four film samples. This independent evaluation of the pore structures would give final confirmation to the other experimental results and provide detailed information about the sizes of the pores present in the coating films. Unfortunately, the determination of total pore volumes and pore distribution analyses by gas adsorption were not completely successful.

The adsorption isotherms obtained for the samples studied indicated that a great many pores larger than 0.1 μ in radius were present (see Fig. 34, Appendix I). Complete pore distributions and total pore volumes cannot be determined accurately by the gas adsorption method for samples having a large number of pores greater than 0.1 μ in radius. A more complete discussion of this point is presented in Appendix I. However, just the indication that there were a substantial number of pores larger than 0.1 μ in the sample films is significant. Starch-clay films of significantly higher void volume or porosity as compared to a pigment film have been found in this study. These large void volumes are visualized in terms of the presence of larger pores, rather than of vast increases in the number of smaller pores. Proof of the existence of large pores lends credibility to the contention that films of such large void volumes do exist.

Although complete pore distribution analyses on the samples were not possible, attempts were made to analyze the changes in the smaller or measurable pores of the four coating samples. The assumptions used for doing this and reference to some of the work in the literature which tends to support the feasibility of the partial analysis of a pore system are discussed in Appendix I (page 125). The pore distribution results obtained in this limited manner for the four samples studied are presented in Fig. 8.

Keeping in mind that only a portion of the pore volumes of the films is being considered (actually less than 50%), definite changes in the pore distributions of the coating samples with increasing starch content can be observed. Between the first two samples, where an increase in total pore volumes occurred, the pore distribution curves in Fig. 8 illustrate that a shift in pore sizes toward larger pores had taken place as was predicted from the total pore volume and surface area results. Although the distribution peaks occur at essentially the same pore radius (0.073 to 0.075 μ), 12.5% of the measurable pores of the first sample were less than 0.03 μ in radius, and only 4.5% were greater than 0.076 μ, while in the second sample the percentage of pores less than 0.03 μ in radius was negligible and 23% were greater than 0.076 μ.

The third and fourth samples, f_{-p} = 0.857 and 0.804, respectively, had narrowing pore distributions (see Fig. 8), thus indicating that both further elimination of small pores and a reduction in the quantity of larger measurable pores had occurred. The results of the pore distribution analysis of the third sample indicated that while the measurable pore volume decreased as compared to the second sample, the remaining pores were such that a shift in pore size distribution toward larger pores occurred. For this third sample, the peak in the distribution curve occurred at about 0.078 μ, and 58% of the pores were between 0.03 and 0.076 μ in radius, while 42% of the pores were larger than 0.076 μ in radius.

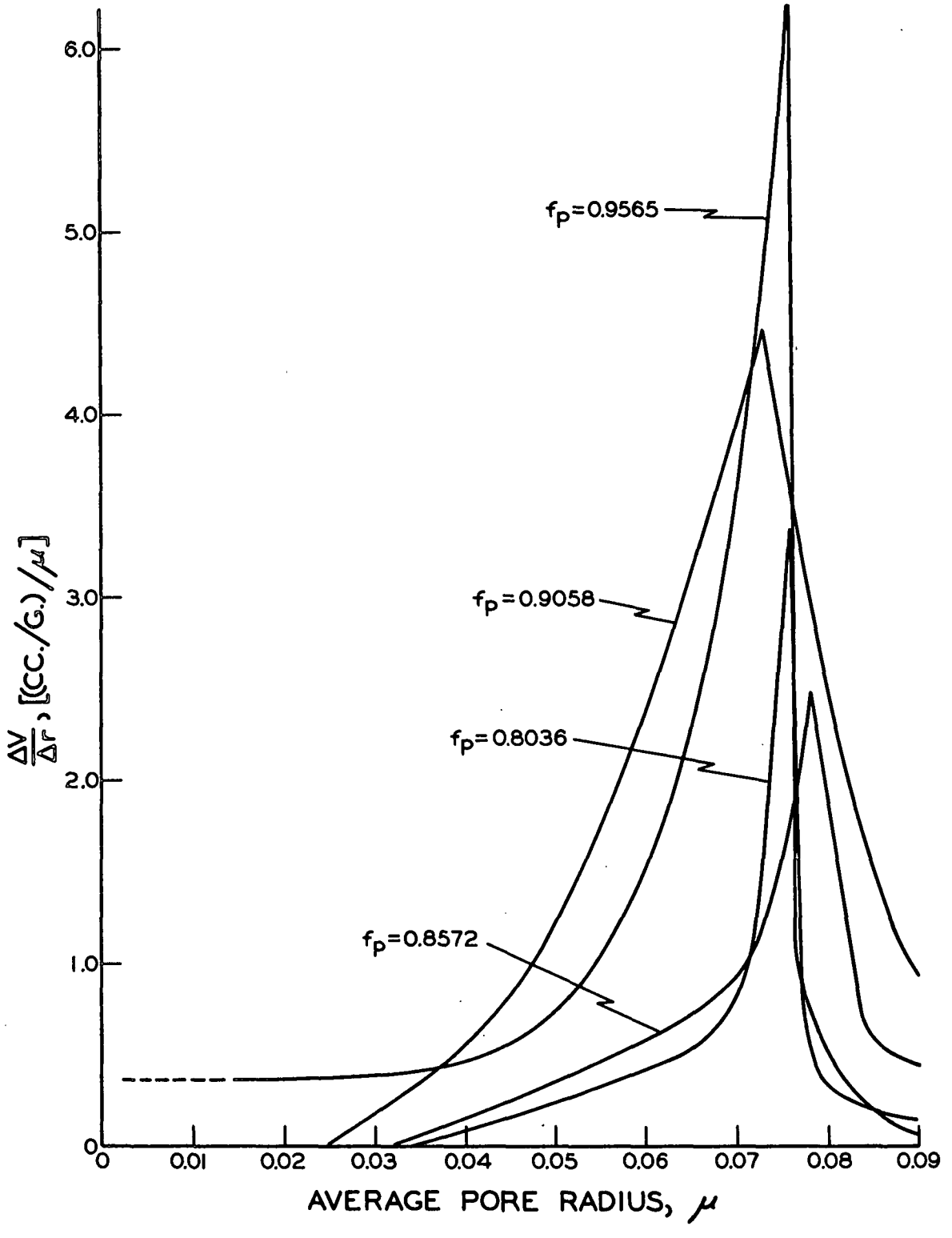


Figure 8. Pore Size Distributions of the Measurable Pores of Selected Starch-Clay Films

These results imply that between the second and third film samples, which correspond, respectively, to the regions of maximum film void volume and maximum skeletal expansion, as denoted in Fig. 5, the decrease in the measurable pores between films is weighted in favor of the elimination of smaller measurable pores.

The pore distribution of the fourth sample was even narrower than that of the third sample, and indicated a shift in pore sizes toward smaller pores. The peak in the distribution curve occurred at 0.075 μ in radius, and 81.5% of the measurable pores were between 0.03 and 0.076 μ in radius. The shift in pore sizes between the last two samples described by the curves in Fig. 8 indicates that the measurable pore volume of the last sample differs from that of Sample 3 mainly in the reduction of pores greater than 0.076 μ in radius.

Because of the changes in the volume of the measurable pores, as represented by the areas under the distribution curves in Fig. 8, there is an opportunity to estimate the contribution of these changes in measurable pore volume toward the changes in total pore volume through the maximum void volume region of the starch-clay films. The data as presented in Fig. 9 are for a comparison of the changes in total film void volumes (calculated from density results) with the changes in measurable void volumes (obtained by integrating the areas under the pore distribution curves in Fig. 8). Direct comparison of the measurable pore volume data points with corresponding total pore volume data illustrates that the measurable pores were a relatively small percentage of the total pore volumes in the films. The majority of the pore volumes in the films studied were composed of pores greater than 0.1 μ radius in size, as indicated previously.

However, comparison of the changes in total pore volumes among films with the corresponding changes in measurable pore volumes indicates that through the maximum void volume range spanned by the films studied, the changes in the smaller

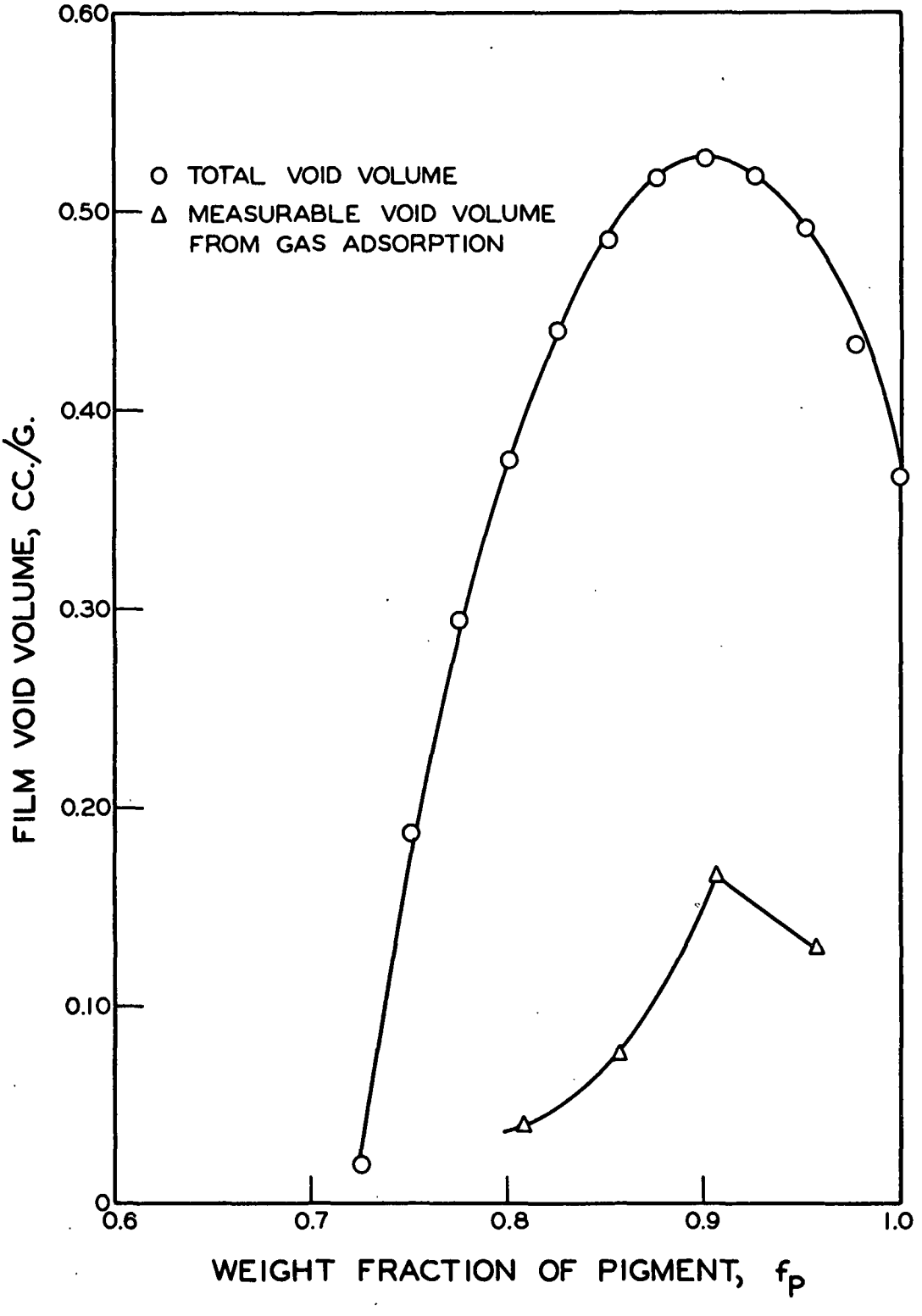


Figure 9. Total Void Volumes and Measurable Void Volumes of Selected Starch-Clay Films

or measurable pores may contribute heavily to the observed behavior of film pore volumes. For example, the change in total pore volume between the first two films studied by gas adsorption was roughly 0.043 cc./g., while the change in volume of the smaller pores was about 0.035 cc./g. Thus, most of the increase in the total pore volume from Film 1 to Film 2 could have occurred through the creation or enlargement of measurable pores. Likewise from the second through the fourth films studied, the decrease in total film pore volumes can be accounted for largely by the decrease in the volume of measurable pores among the films. Actually, the change in the measurable pore volume of 0.094 cc./g. between the second and third samples was greater than the overall change in total pore volume between the samples, and thus some larger pores must have been created to offset the difference between the changes in total and measurable pore volumes. This is quite reasonable because, as was pointed out earlier, the pigment skeleton was still being expanded between the second and third samples, and thus, although the total void volume was decreased, some larger pores (greater than 0.1 μ in radius) could have been created.

As has been discussed, the measurable pores in the samples studied are a relatively small percentage of the total pore volumes, and it is the change in number of pores greater than 0.1 μ in radius which accounts for most of the change in void volumes among the porous starch-clay films. Throughout the regions of rapid skeletal expansion and compaction, it is the creation and destruction of these large pores which are believed to occur with changes in starch content.

Microscopic Examination of Film Pores

The presence of large pores in the starch-clay films studied here, as shown in the preceding experimental work, was confirmed microscopically. A cross section of the film $f_p = 0.857$, which had been studied by gas adsorption and which

was close to the region of maximum expansion of the film pigment skeleton, was examined with the aid of the electron microscope. This cross section is shown in Fig. 10. Many pores larger than 0.1 μ in radius can be observed, and pores greater than 1.0 μ in diameter appear to be present. Considering the size of the clay particles involved, this is evidence that the pigment skeleton of the film has been expanded by the starch present so as to yield a more porous structure than would ever be possible in an unbonded clay pigment film. The observation of these large pores adds visual evidence that the clay platelets do not pack independently of the starch present.

Two other film cross sections were also studied visually. These films were selected from the regions both of film skeletal compaction and of film densification. Electron micrographs of these cross sections are shown in Fig. 11 and 12. Careful examination and comparison of all three cross sections confirm the densification of the films with increasing starch content and show that a reduction in size of the larger pores present in the films accompanies the compaction of the pigment skeleton of the films. However, some pores of approximately 1.0 μ diameter still exist in the two films of higher starch content.

Particle Orientation Studies on Starch-Clay Films

The preceding experimental work in this study has shown that the pigment skeleton of starch-clay films was altered by changes in starch content. Possible measurable changes among films in the relative positions of clay platelets within the pigment skeleton were investigated by the particle orientation technique, which was described in the Experimental Procedures. While expansion or compaction of the pigment skeleton may or may not be accompanied by measurable changes in the relative positions of clay platelets, evidence of such changes would add more support to the contention that the starch present in the films is affecting the

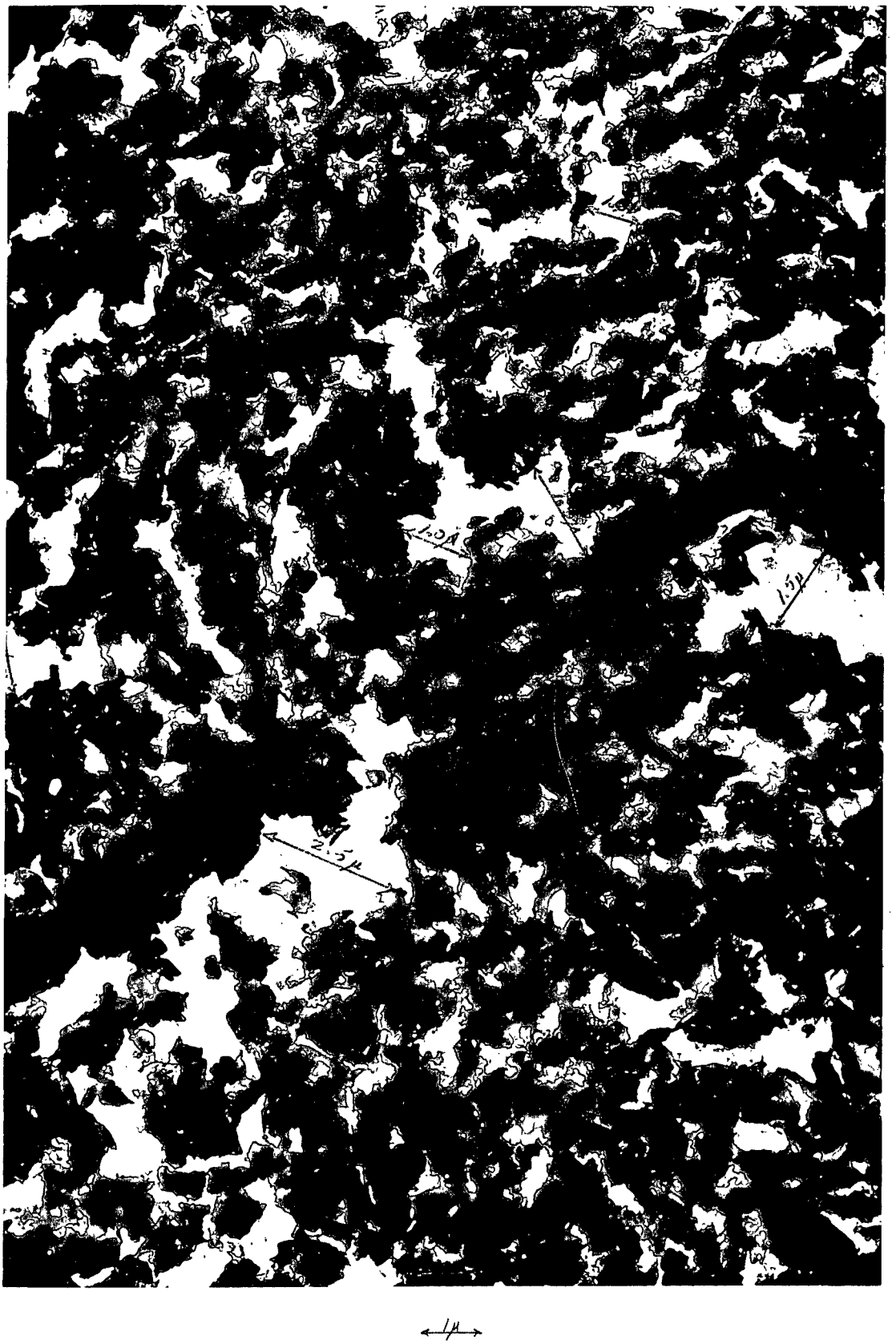


Figure 10. An Electron Micrograph (9000X) of a Cross Section of a Starch-Clay Film of $f_{-p} = 0.857$ Formed on a Nonporous Substrate

Figure 11. An Electron Micrograph (9000X) of a Cross Section of a Starch-Clay Film of $f_{-p} = 0.804$ Formed on a Nonporous Substrate

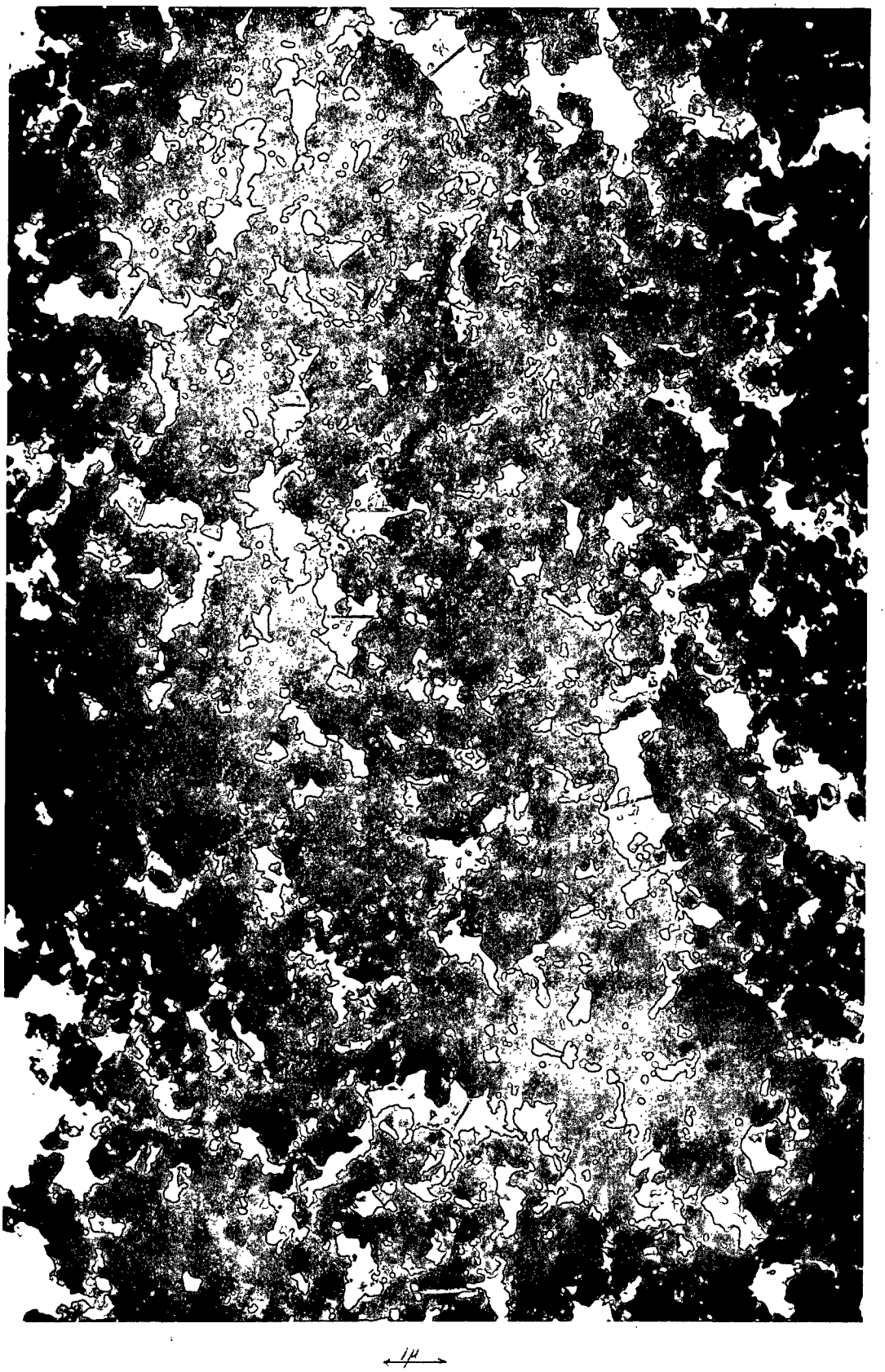


Figure 12. An Electron Micrograph (9000X) of a Cross Section of a Starch-Clay Film of $f_{-p} = 0.744$ Formed on a Nonporous Substrate

packing of the pigment particles, and should help contribute to the overall picture presented to describe the effect of the starch on pigment-adhesive film structures.

A plot of the measured orientations of selected starch-clay films versus the weight fraction of the pigment in the films is presented in Fig. 13. The data used to determine the particle orientation profiles of the individual films are given in Appendix II, Tables VII and IX. When looking at Fig. 13, it will be helpful to remember that the higher the numerical orientation value, or the more negative the value, the greater the degree of platelet orientation or alignment parallel to the plane of the substrate upon which the film was formed.

The measured particle orientations of the starch-clay films, as shown in Fig. 13, decreased with initial amounts of starch and passed through a minimum. The orientation values ranged from about -4.1 for a film of $f_p = 0.962$, down to a minimum orientation value of about -2.8 at $f_p = 0.845$. Previous experimental data on these films, as presented in Fig. 5 and 7, have been interpreted to show that the pigment skeleton of the films was expanded by increases in starch content from $f_p = 1.0$ to $f_p = 0.85$. Thus, decreases in film particle orientations, and hence disruptions in the alignment of clay platelets parallel to the plane of the substrate, were coincident with film skeletal expansion.

The point of minimum measurable orientation or maximum disruption of platelets relative to the substrate occurred at roughly the same weight fraction pigment ($f_p = 0.85$) as the maximum skeletal expansion of the starch-clay films, designated as Point C in Fig. 5. After the point of minimum platelet orientation in films, further increases in starch content caused increased orientation. These increases continued throughout the porous film region, reaching a value of about -3.9 at $f_p = 0.744$. Interpretation of previous experimental data, as in Fig. 5 and 7, has shown that a compaction of the pigment skeleton of the starch-clay films occurred between $f_p = 0.85$ and $f_p = 0.725$, the end of the porous film

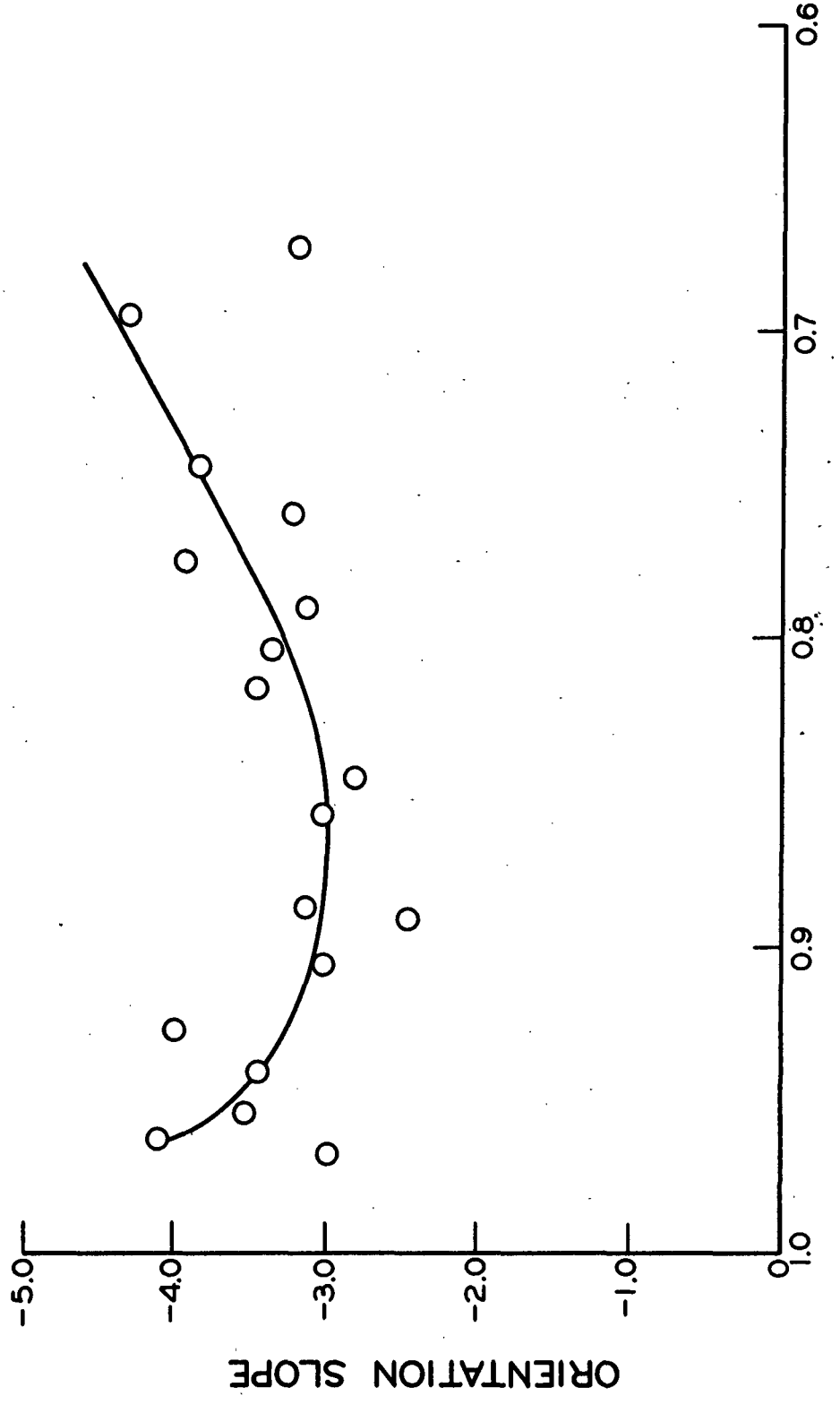


Figure 13. Effect of Changes in Weight Fraction of Pigment, f_p, on Film Particle Orientations of Starch-Clay Films

region. This compaction therefore was coincident with increases in the measurable orientation of clay platelets within films. Although not enough data are present to be conclusive, the orientation value of -4.3 at f_p = 0.69 suggests that alignment of the clay platelets parallel to the plane of the substrate might continue into the continuous film region.

A POLYVINYL ALCOHOL-CLAY FILM SYSTEM

Films were also prepared on tinfoil from coating colors containing varying ratios of PVA and clay. The specific volumes of these films are plotted versus the weight fraction of pigment of the films in Fig. 14. These data are tabulated in Appendix III, Table XI. The straight lines representing the idealized void filling model in Fig. 14 are constructed from the specific volume of the PVA (0.791 cc./g.), the specific volume of the clay (0.385 cc./g.), and the specific volume of a film containing only clay (0.74 cc./g.) in the same manner as already described with reference to Fig. 5 in the preceding section. Film void volumes and total film volumes per gram of clay were calculated from specific volume and composition data at chosen points along the experimental specific volume curve obtained in Fig. 14 and plotted in Fig. 15 and 16, respectively. These three plots for the PVA-clay system are therefore directly comparable to Fig. 5, 6, and 7, respectively, for the starch-clay system.

It is apparent from the data in Fig. 14 that the specific volumes of the PVA-clay films do not correspond with the prediction of the idealized void-filling model. The data points show a sharp maximum at very low PVA levels. It is not feasible from the data to determine the point of maximum specific volume (A') for the PVA-clay film system, but it appears to occur at a value equal to or greater than f_p = 0.98 (2.2 parts PVA per 100 parts clay). This film at f_p = 0.98, having a specific volume of 0.87 cc./g., corresponds to the film of the highest pigment content which contained PVA that was studied.

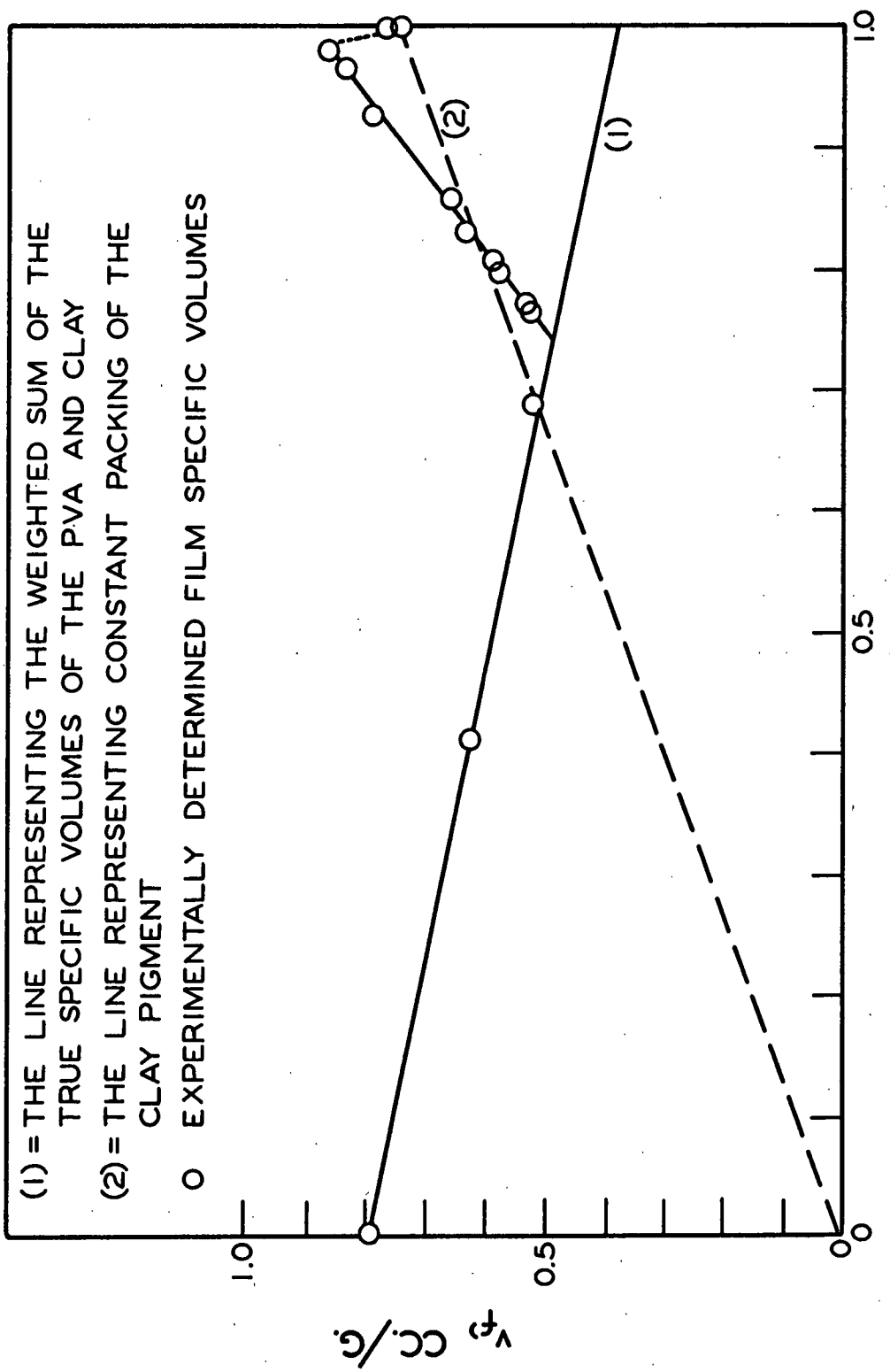


Figure 14. Effect of Changes in Weight Fraction of Pigment, f_p, on Film Specific Volume, v_f, of PVA-Clay Films

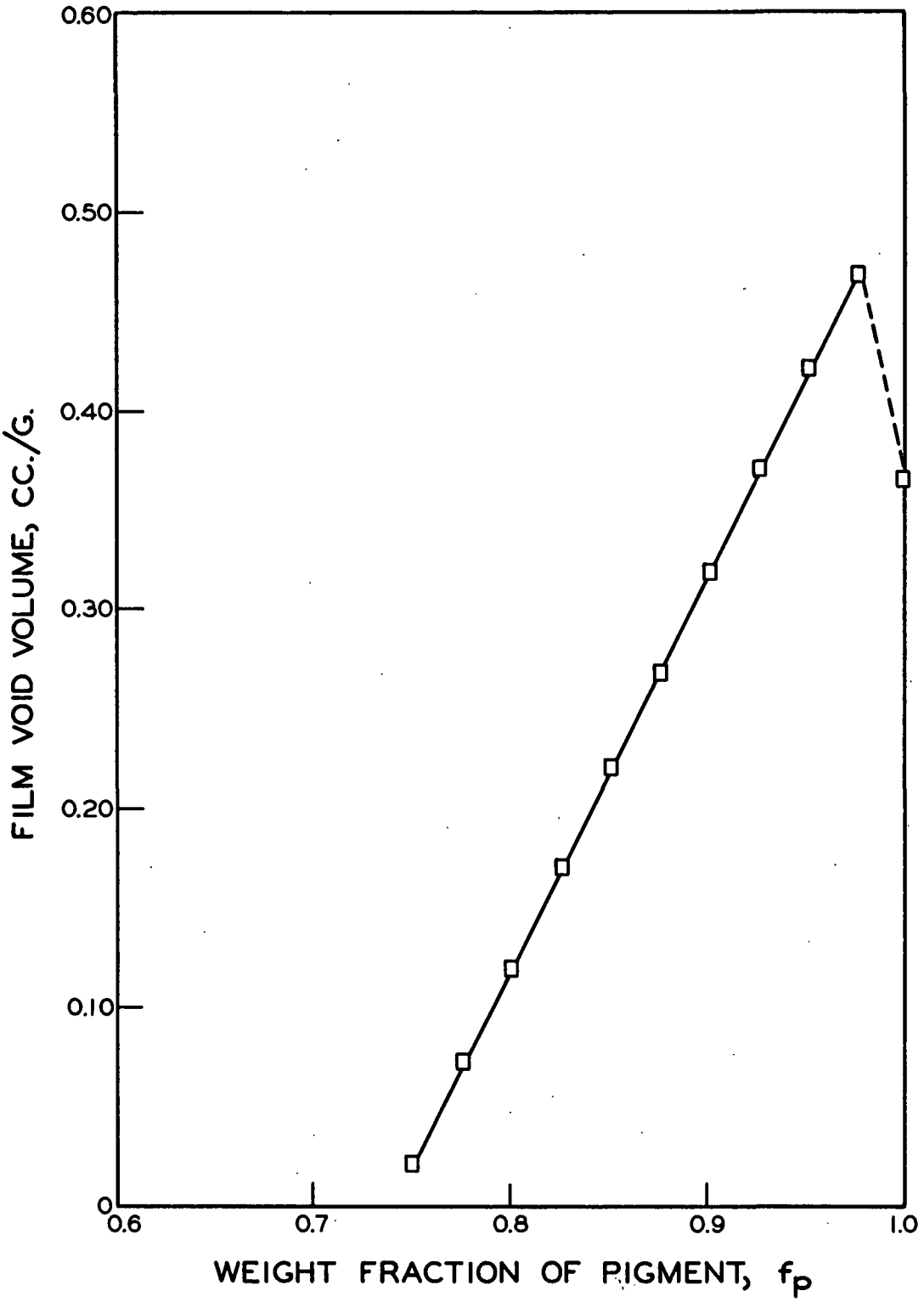


Figure 15. Changes in Film Void Volume with Changes in Weight Fraction of Pigment, f_p, for PVA-Clay Films

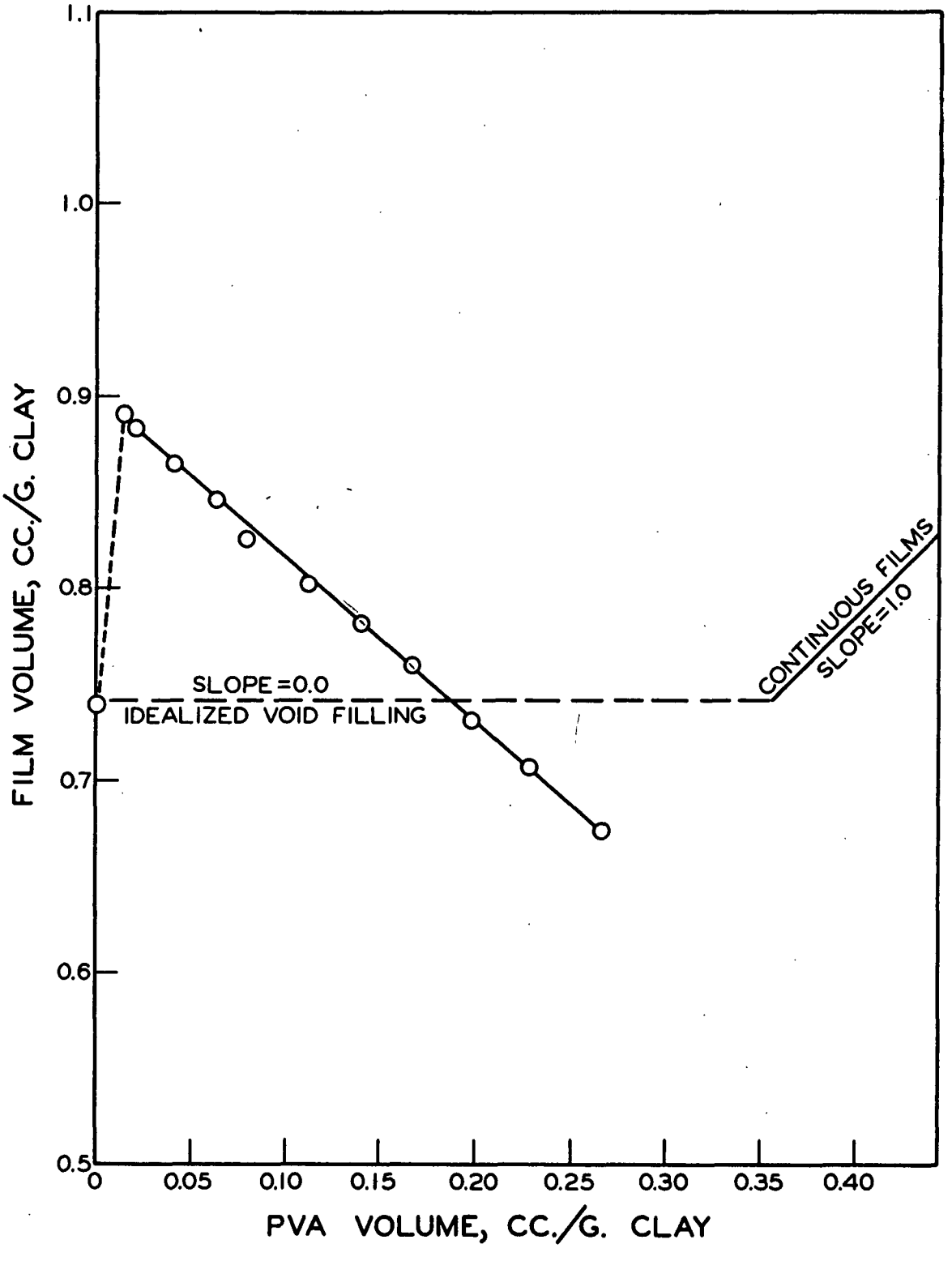


Figure 16. Changes in Film Volume per Gram of Clay with Changes in PVA Volume per Gram of Clay

The maximum in the data points observed in Fig. 14 may be interpreted to show that maxima in film void volume and pigment skeletal expansion must occur in the PVA-clay system. However, just as it is not possible to define accurately the point of maximum specific volume (A'), it is not possible to establish the point of maximum void volume (B'), or the point of maximum skeletal expansion (C'), because of the limited data for films of very low binder content. Because of the sharpness of the peak in the available specific volume data, it can be expected that these three maximum values, while theoretically not coincident, must lie very close together.

There were definite similarities in the PVA-clay and starch-clay film systems. Both systems exhibited a large degree of pigment skeletal expansion at lower adhesive contents, thus causing maxima in film void volumes and specific volumes to occur. Then, further increases in adhesive levels caused a compaction of the pigment skeletons to take place, and film void volumes and specific volumes were decreased to a much greater degree than possible by adhesive void filling alone. Just prior to reaching a continuous film, the PVA-clay films, like the starch-clay films, showed greater densities or lower specific volumes than could ever have been obtained by idealized void filling of the original pigment film. Continuous films of both film systems were described by the weighted sum of the specific volumes of the adhesive and the clay.

There were also very distinct differences between the PVA-clay and starch-clay film systems. The points of maximum skeletal expansion, void volume, and specific volume of the PVA-clay films, although not absolutely defined in this study, must occur at much lower adhesive levels than in the starch-clay system. The rates of skeletal compaction with changes in adhesive contents, as may be estimated from the data in Fig. 7 and 16, were different. The rate of skeletal

compaction of the PVA-clay films was fairly constant up to the formation of a continuous film as opposed to the increasing rate of starch-clay skeletal compaction. Finally, the onset of a continuous film, or the C.P.V.C., occurred at $f_{-p} = 0.74$ for the PVA-clay system as opposed to an ideally predicted value of $f_{-p} = 0.645$, while the C.P.V.C. for the starch-clay films was at $f_{-p} = 0.725$.

Particle Orientation Studies on the PVA-Clay Film System

Particle orientation studies on selected PVA-clay films were made to determine if any measurable changes in the relative positions of clay platelets within the pigment skeleton occurred as a result of the expansion and compaction of the skeleton, which was shown by the preceding experimental work. A plot of the measured particle orientations of PVA-clay films versus the weight fraction of the pigment in the films is presented in Fig. 17. The data used to determine the particle orientations of the films are given in Appendix III, Tables XII and XIII.

Because there were no PVA-clay film samples in the expanding skeletal region, the films studied began with the film of maximum expansion detected for the system, and continued throughout the region of skeletal compaction with increasing PVA. If it is assumed that the orientation values obtained for starch-clay films of low starch content and low degree of skeletal expansion (orientation value of -4.1 at $f_{-p} = 0.962$) approach the measurable orientation of a clay pigment film containing no adhesive, then it may be proposed that the initial amounts of PVA decreased the measurable particle orientation of PVA-clay films to the value of -2.5 determined for the film of maximum observed skeletal expansion. The feasibility of this supposition should become more apparent when mechanisms are proposed to explain skeletal expansion of PVA-clay and starch-clay films.

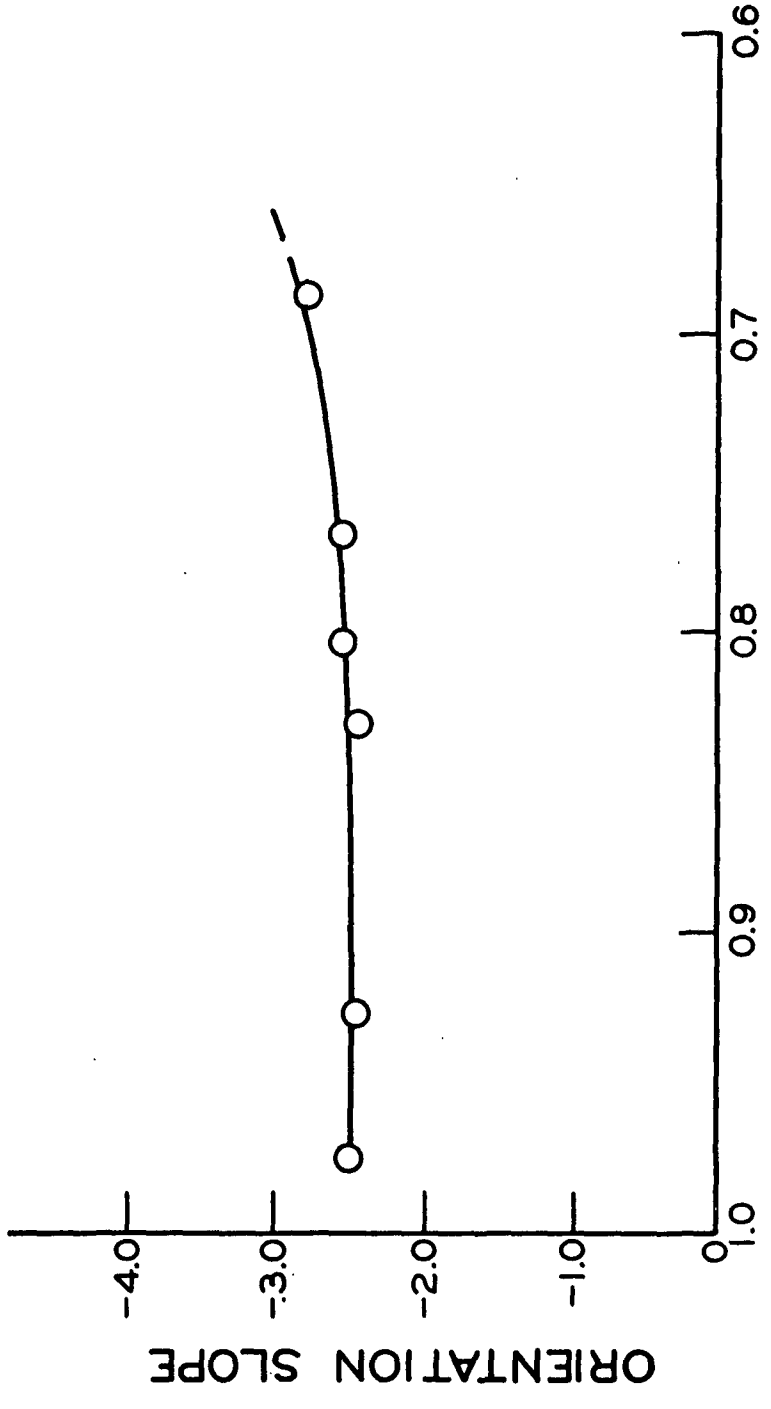


Figure 17. Effect of Changes in Weight Fraction of Pigment, f_p, on Film Particle Orientations of PVA-Clay Films

The data presented in Fig. 17 show that the particle orientation values of the films, which ranged from about -2.5 at $\underline{f}_p$ = 0.978 to -2.8 at $\underline{f}_p$ = 0.687, did not increase to a large degree with increasing PVA. The previous experimental data on these films, as presented in Fig. 14 and 16, have been interpreted to show that the pigment skeleton of the films was being compacted from $\underline{f}_p$ = 0.978 to $\underline{f}_p$ = 0.687. Thus, compaction of the PVA-clay pigment skeleton was not accompanied by large increases in the degree of measurable clay platelet orientation relative to the substrate, as was the case for starch-clay films.

It should be pointed out that structural compaction need not be accompanied, necessarily, by a high degree of platelet alignment parallel to the substrate at higher adhesive levels. This point will be expanded upon, and a means proposed to explain platelet compaction without high orientation relative to the substrate, when a mechanism is proposed for the means by which PVA affects film structure.

A LATEX-CLAY SYSTEM ON A NONPOROUS SUBSTRATE

The final series of films containing varying latex-clay ratios was prepared on the nonporous foil substrate. The specific volumes of the latex, the clay, and the latex-clay films, and the specific volume of a pigment film containing no latex are presented in Fig. 18 in the manner previously described for evaluating the hypothesis of idealized adhesive void filling. The specific volumes of the latex and clay were 0.990 cc./g. and 0.385 cc./g., respectively, and the clay pigment film had a specific volume of 0.74 cc./g. The specific volume data for the latex-clay films are tabulated in Appendix IV, Table XIV.

The specific volumes of the latex-clay films, as shown in Fig. 18, decreased continually with increasing latex in the porous film region, but not along the idealized void-filling line. At any given weight fraction of pigment, the experimentally determined film specific volumes were higher than predicted by idealized

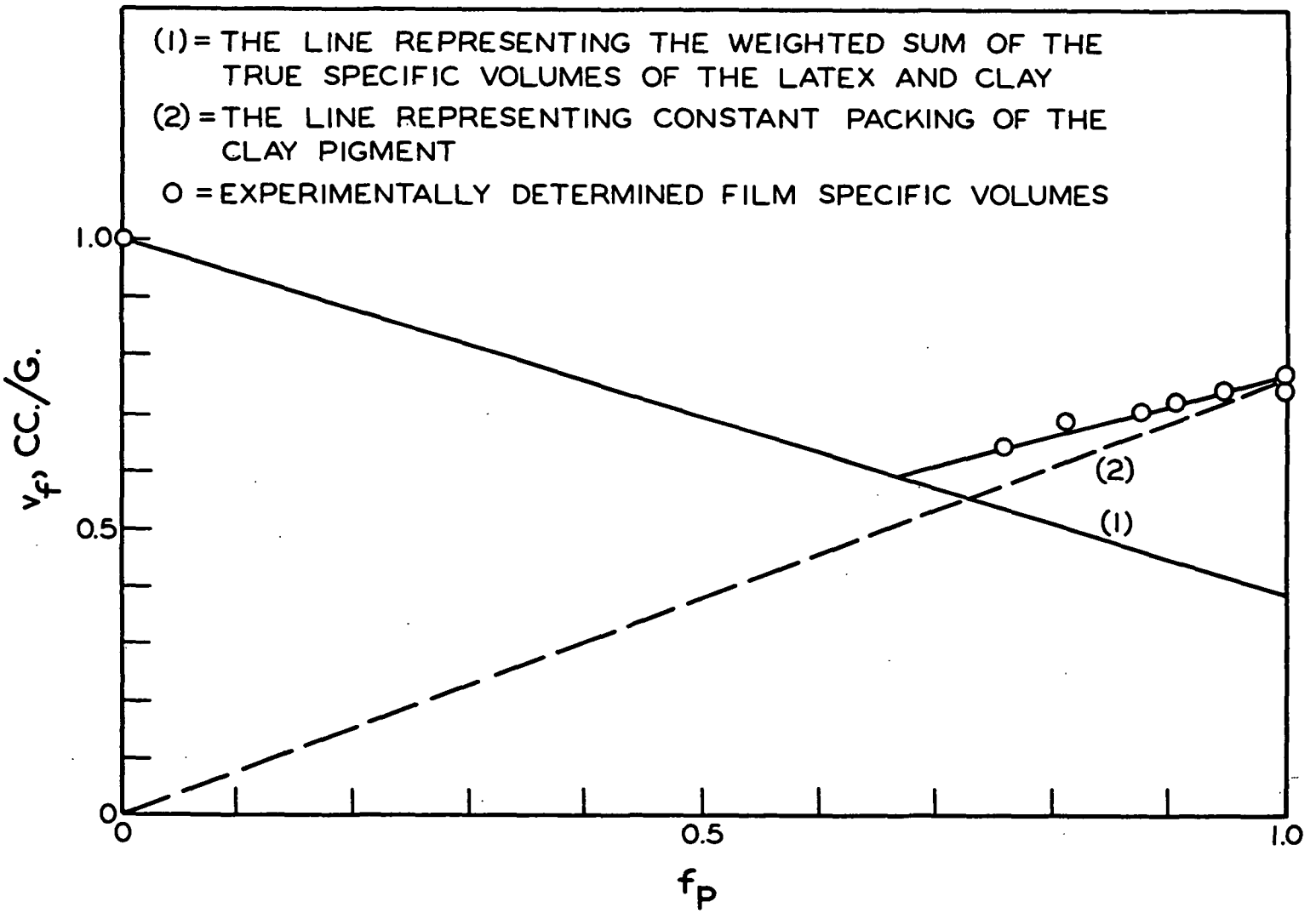


Figure 18. Effect of Changes in Weight Fraction of Pigment, f_p, on Film Specific Volume, v_f, of Latex-Clay Films

void filling, and the divergence between experimental specific volumes and the idealized void-filling line increased with increasing latex up to a continuous latex-clay film. There was no maximum in film specific volume with increasing binder as occurred in the other two pigment-adhesive systems already discussed (Points A and A' for the starch-clay and PVA-clay systems, respectively).

Evaluation of the vertical distance between the experimental specific volume line and the continuous film line at any weight fraction of pigment in Fig. 18 shows that film void volumes, cc./g., decreased with increased latex, and therefore there was no maximum in film void volume with increased binder content as was found in the other two pigment-adhesive systems (Points B and B' for the other two systems). This steady decrease in film void volume with increased latex may be emphasized by replotting experimental points selected from the specific volume curve in Fig. 18 as film void volume versus weight fraction of pigment, as is done in Fig. 19.

The results shown in Fig. 18 may be interpreted to show that the deviation of the latex-clay system from idealized void filling must be due to an expansion of the film pigment structure by the latex. The pigment skeleton of the latex-clay films was expanded continually throughout the porous film region by increases in latex content. The expansion of the pigment skeleton of the latex-clay films can also be shown by replotting selected data points from the experimental curve in Fig. 18 as film volume per gram of pigment versus latex volume per gram of pigment, as is done in Fig. 20. This figure is constructed in the same manner as Fig. 7 and 16 for the starch-clay and PVA-clay films, respectively. The slope of the experimental line in Fig. 20 is positive and less than 1.0, which confirms that while film structure expanded, film void volume was decreased.

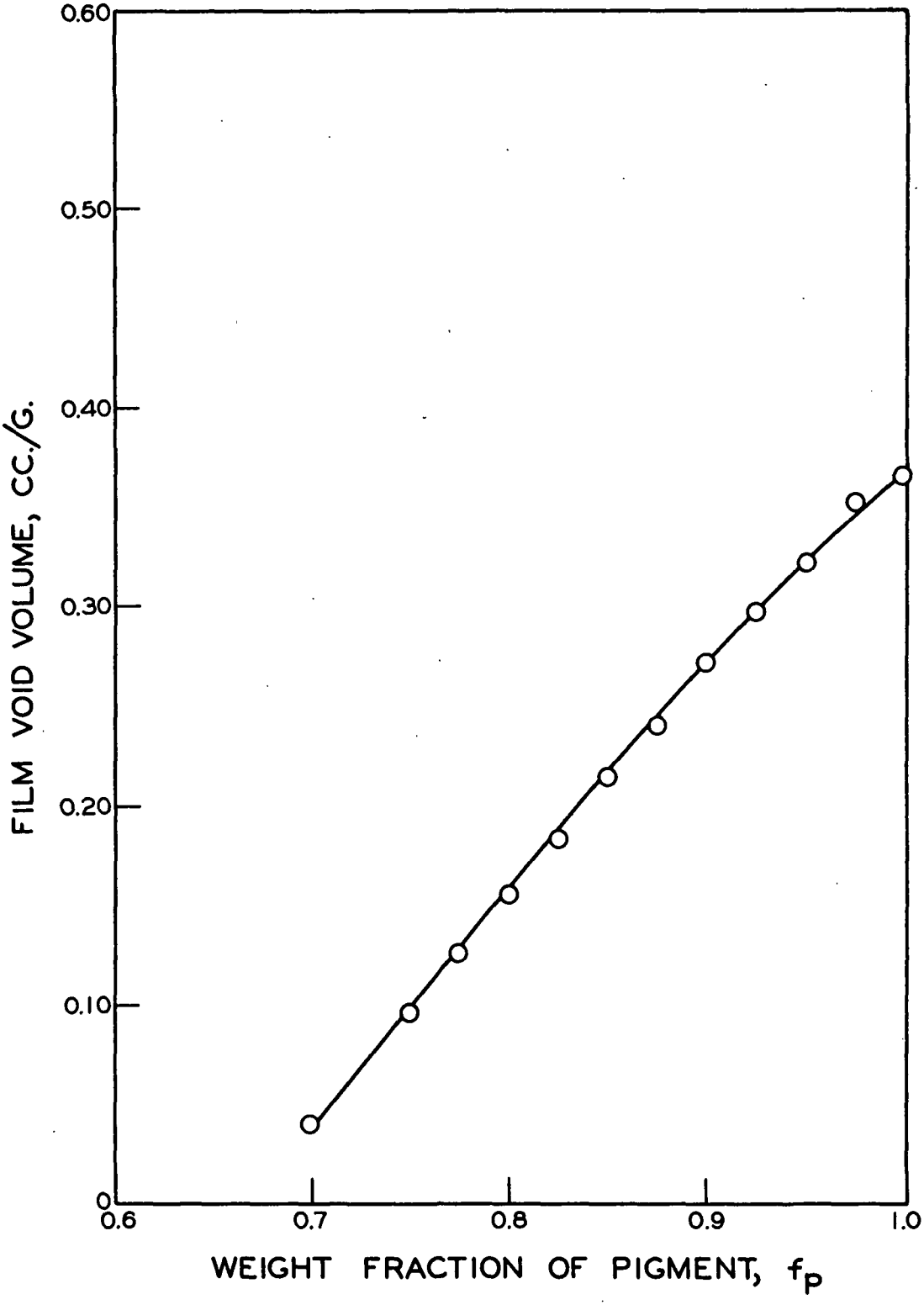


Figure 19. Changes in Film Void Volume with Changes in Weight Fraction of Pigment, f_p, for Latex-Clay Films

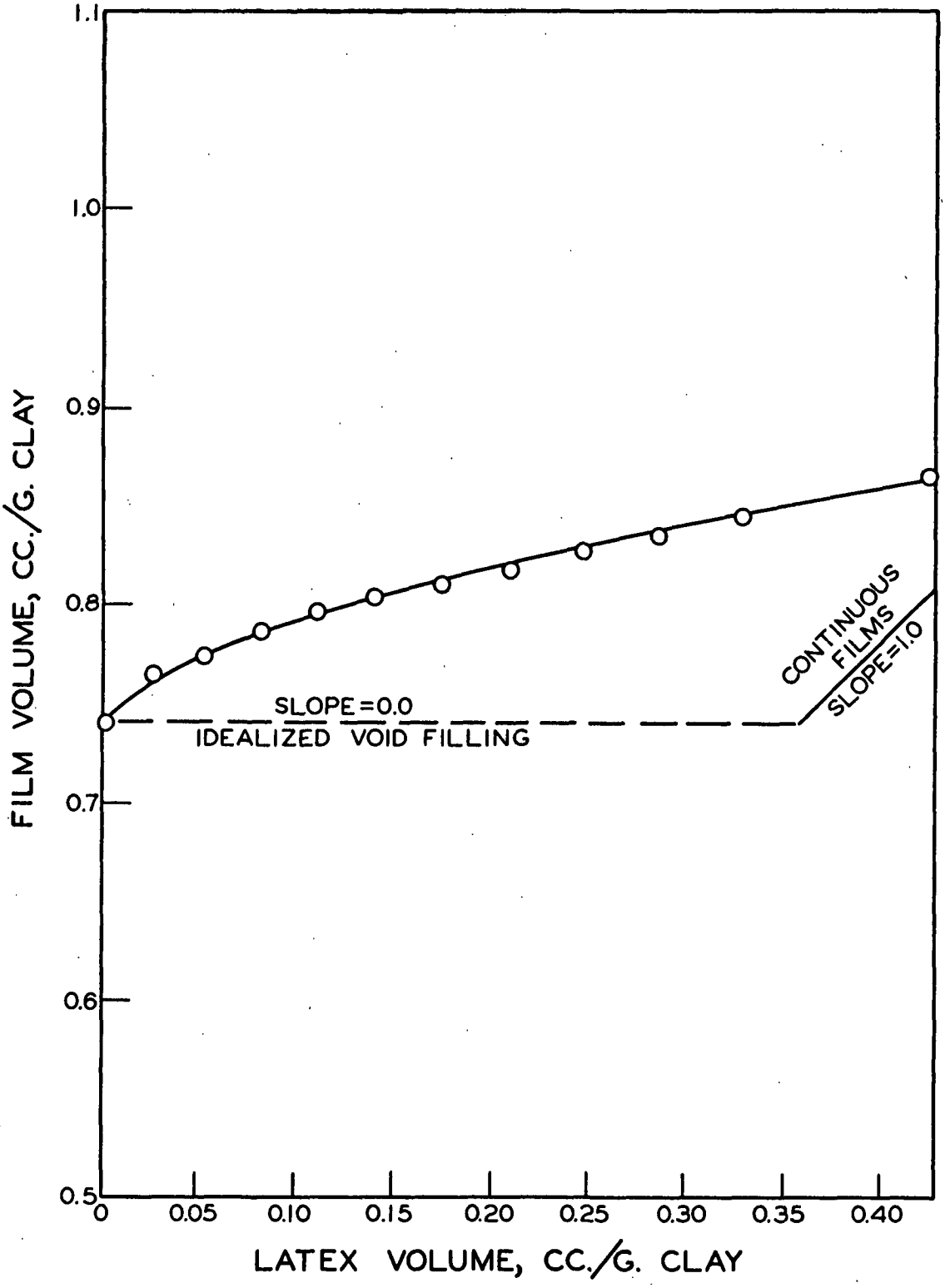


Figure 20. Changes in Film Volume per Gram of Clay with Changes in Latex Volume per Gram of Clay

Particle Orientation Studies on the Latex-Clay System

The particle orientations of several of the latex-clay films were determined to ascertain if the expansion of the pigment skeleton of the films, which was shown to occur throughout the porous film region, caused any measurable changes in the alignment of the clay platelets among films. Figure 21 is a plot of the orientation values of the latex-clay films versus the weight fraction of pigment of the films. The data used to determine the particle orientations of the latex-clay films are given in Appendix IV, Tables XV and XVI.

The orientation value of -2.6 obtained from the latex-clay film of the lowest latex content studied ($f_{-p} = 0.944$) was quite low compared to the orientations observed for starch-clay films at very low starch levels (for starch from $f_{-p} = 0.962$ to $f_{-p} = 0.906$, orientation values ranged from -4.1 to -3.0, respectively). If one assumes that the orientations of the starch-clay films of low starch content and slight skeletal expansion approach the orientation of a clay pigment film, then the initial amounts of latex added to the pigment in forming latex-pigment films caused significant disruptions in the alignment of the clay platelets and thus reduced measurable particle orientation.

Further addition of latex binder caused increases in the measurable orientation of the latex-clay films, as shown by the data in Fig. 21, from the minimum value of -2.6 at $f_{-p} = 0.944$ to a value for the film of highest latex content studied, $f_{-p} = 0.756$, of -3.89. Since the results of Fig. 18 and 20 have been interpreted to show skeletal expansion for the latex-clay films over the entire porous film region, this increase in the measurable orientation of the clay particles among films from $f_{-p} = 0.944$ to $f_{-p} = 0.756$ coincided with skeletal expansion in the films. This was quite different from the behavior in the other two pigment-adhesive systems where it was suggested that skeletal expansion decreased orientation and that it was skeletal compaction which was accompanied by increased measurable orientation.

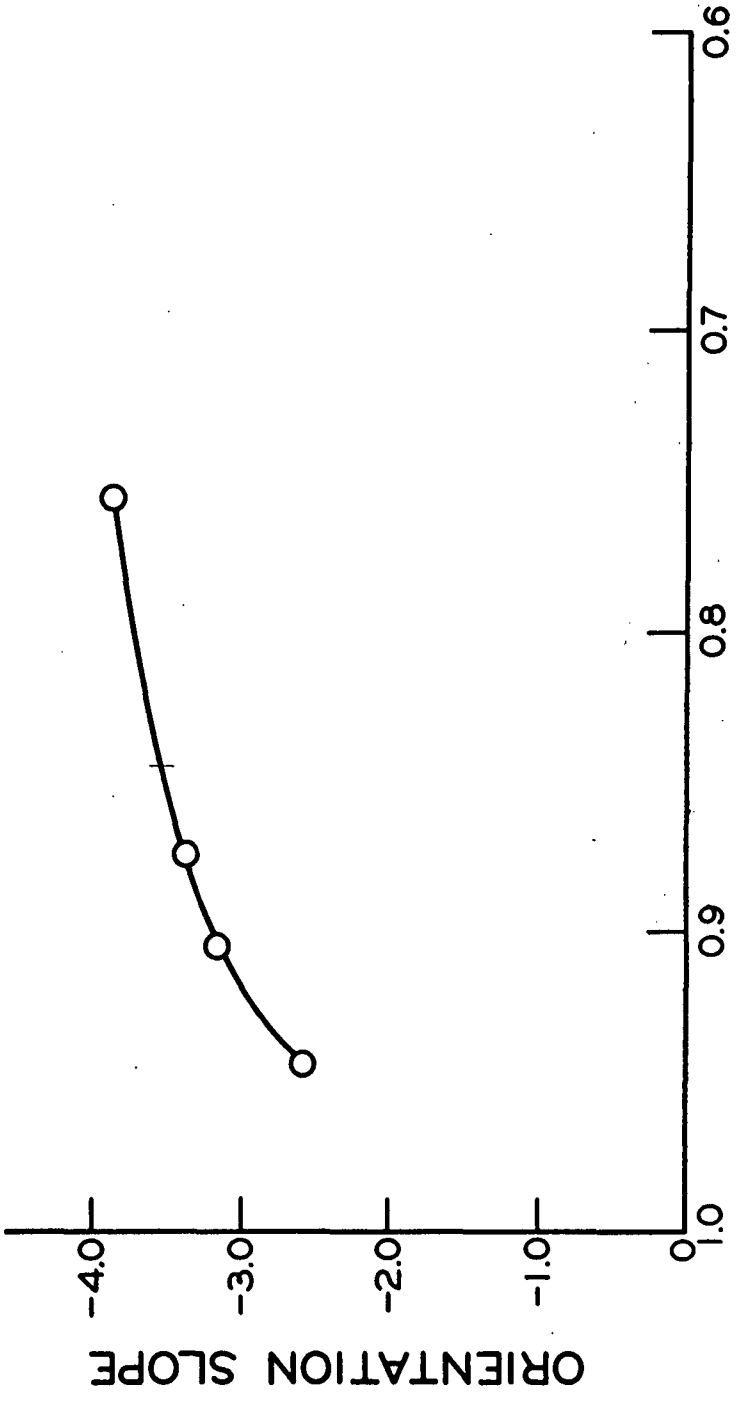


Figure 21. Effect of Changes in Weight Fraction of Pigment, f_p, on the Particle Orientations of Latex-Clay Films

A means by which the latex could first decrease measurable particle orientations and then cause simultaneous film expansion and increased orientation to occur will be suggested in the discussion of a mechanism by which latex affects film structure. However, regardless of the means by which they occur, changes in particle orientations among films are substantiating evidence that the packing of the clay platelets in the pigment skeleton was affected by the presence of the latex.

A PIGMENT-ADHESIVE FILM SYSTEM ON A POROUS SUBSTRATE

A STARCH-CLAY FILM SYSTEM ON A POROUS SUBSTRATE

The starch-clay coating system which had been applied previously to the nonporous foil substrate was also applied to a porous substrate. The purpose here was to determine the extent to which substrate porosity might influence film structural formation. Therefore, structures of starch-clay films formed on the porous and nonporous substrates were compared.

The specific volumes of the starch-clay films formed on a porous substrate are plotted in Fig. 22 in the manner which is used in this study for evaluating idealized void filling. The straight lines shown in Fig. 22, which again describe the idealized void-filling model, are constructed from the specific volumes of the starch (0.674 cc./g.), the clay (0.385 cc./g.), and a clay pigment film containing no starch (0.71 cc./g.). The method of construction and the significance of the void-filling model are the same as discussed earlier in connection with Fig. 5. The specific volume data of the starch-clay films are tabulated in Appendix V, Table XVII.

The specific volume value of 0.71 cc./g. obtained for a clay pigment film formed on a porous substrate was slightly lower than that for the pigment film formed on a nonporous substrate. It is difficult to say whether a real difference

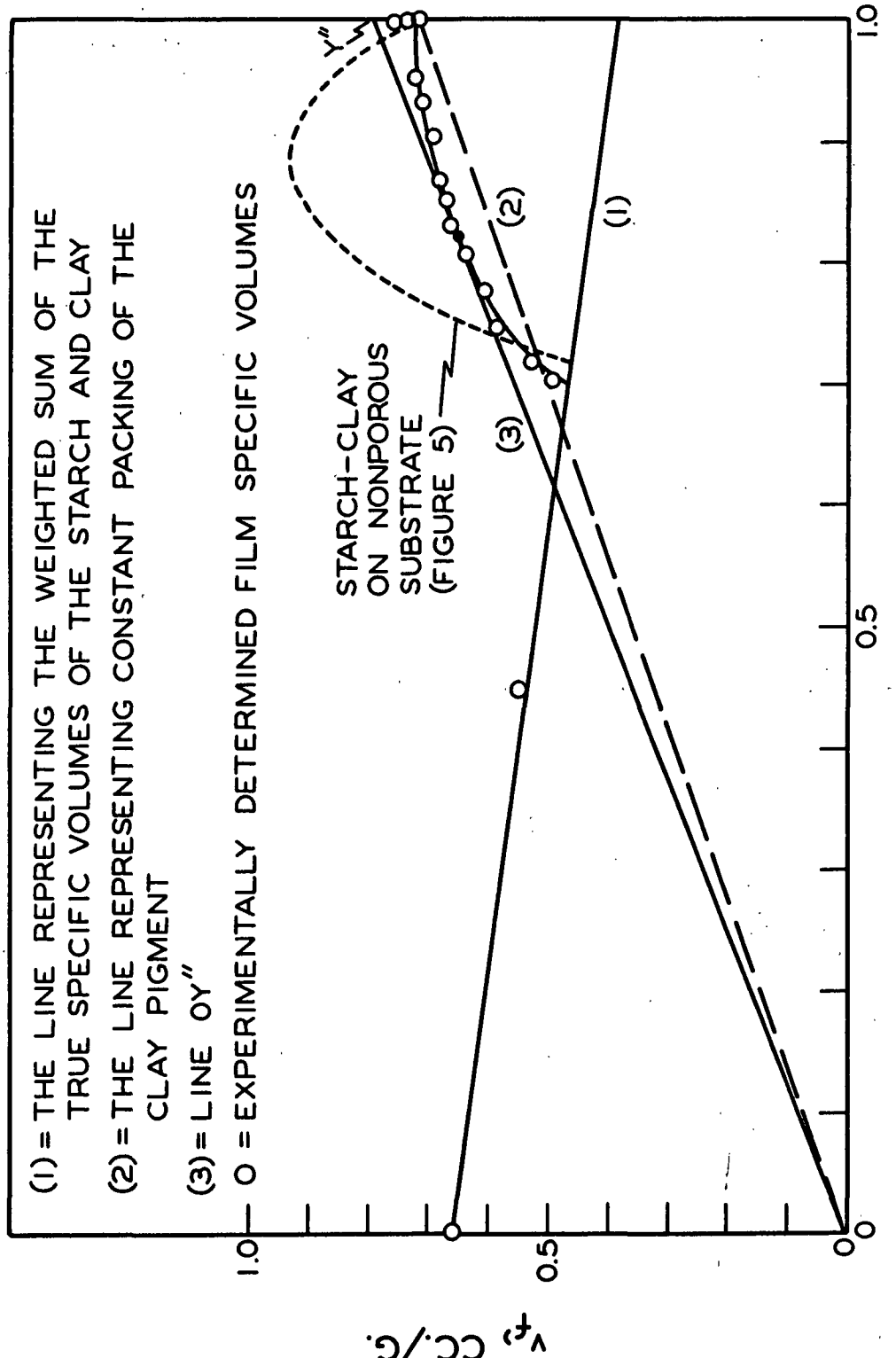


Figure 22. Effect of Changes in Weight Fraction of Pigment, f_p, on Film Specific Volume, v_f, of Starch-Clay Films Formed on a Porous Substrate

in specific volumes between the films exists or whether the difference is merely experimental error due to the difficulties involved in determining the specific volume of a 100%-pigment film.

It seems pertinent to point out that the experimental results for the films formed on a porous substrate are based upon the composition of the dried coating films which were isolated for study. That is, the starch content reported for the films is the actual starch present in the films and does not include the starch lost from the coating colors due to substrate migration.

The specific volume data points for starch-clay films presented in Fig. 22 do not fall along the idealized void-filling line. However, film specific volumes did decrease steadily with increasing starch, and at no point over the porous film region was there an increase in film specific volume with increasing starch, as was the case when starch-clay films were formed on a nonporous substrate. The curve drawn through the film specific volumes shows a maximum deviation from the idealized void-filling line over a fairly broad starch range ($f_{\underline{p}}$ = 0.85 to 0.80). This deviation is indicated in Fig. 22 by the vertical distance between the experimental curve and the void-filling line at any weight fraction of pigment. After exhibiting this maximum deviation, the experimental specific volume data coverage toward the idealized void-filling line, and just prior to the continuous-film region, the curve connecting the data points crosses and drops below the void-filling line, thus indicating that films of lower specific volume occurred than could ever be obtained by idealized void filling of the pigment film. A continuous film was obtained at $f_{\underline{p}}$ = 0.700 as compared to the value predicted by idealized void filling of $f_{\underline{p}}$ = 0.645. The continuous starch-clay films were described again by the weighted sum of the specific volumes of the components.

Once again in Fig. 22, the vertical distance between the experimental specific volume curve and the continuous starch-clay film line represents the void volume of a film at any given weight fraction of pigment. The void volumes of the films showed continual decreases with increasing starch content. There was no point of maximum film void volume with increasing starch as was shown for the starch-clay system on a nonporous substrate. For clarity, the void-volume data at chosen points along the experimental specific volume curve were replotted in a form shown in Fig. 23, which corresponds to Fig. 6 for the system on a nonporous substrate.

Further examination of the data in Fig. 22 shows the manner in which the starch content affected the pigment matrix of the starch-clay films. The family of lines again may be constructed in Fig. 22 from the origin, through points on the experimental curve, to the specific volume axis at $f_p = 1.0$. The intercepts of these lines may be used to examine the expansion and compaction of the pigment skeleton with different amounts of starch, as was done for the starch-clay system on the nonporous substrate (see page 39 of this thesis). An analysis of the data by this means shows that the pigment skeleton of the starch-clay films was expanded by initial increments of starch, passed through a maximum, and then was compacted by further increases in starch until a continuous starch-clay film was reached. Maximum skeletal expansion, designated at Point C" in Fig. 22, was at a weight fraction pigment of 0.825, and corresponded to Point C in Fig. 5 for the system on a nonporous substrate. Maximum skeletal expansion for films on the porous substrate coincided with the maximum deviation in film specific volumes from the prediction of idealized void filling.

The starch level at which maximum expansion of the pigment skeleton took place for films on the porous substrate was very close to that level at which maximum expansion occurred on the nonporous substrate, and with better definition

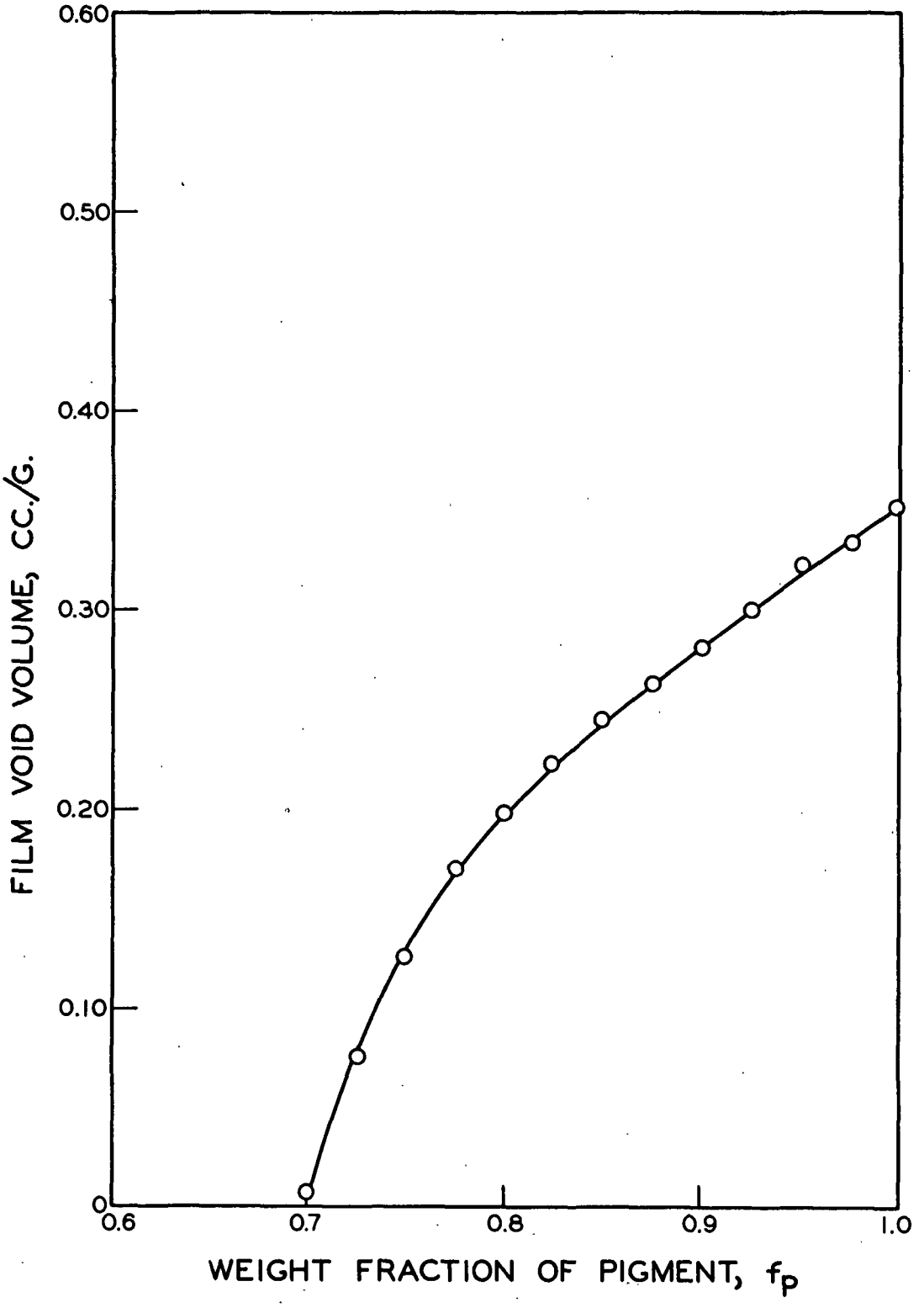


Figure 23. Changes in Film Void Volume with Changes in Weight Fraction of Pigment, f_p, for Starch-Clay Films Formed on a Porous Substrate

of the experimental specific volume curves in Fig. 5 and 22, the maxima might actually occur at the same weight fraction of pigment. The relationship between the points of maximum skeletal expansion of starch-clay films on porous and nonporous substrates is more clearly shown by replotting the data from films on the porous substrate as shown in Fig. 24. Figure 24 is comparable to Fig. 7 for starch-clay films on a nonporous substrate. It can be seen in Fig. 24, upon which is superimposed the data from Fig. 7 for ease of comparison, that the points of maximum skeletal expansion of starch-clay films formed on porous and nonporous substrates occur at essentially the same starch level (18 to 21 parts starch/100 parts clay on a weight basis).

The method of presenting the data as in Fig. 24 again has the advantage of allowing estimates of the rate of skeletal change with increasing amounts of starch. The slope of the curve up to the point of maximum skeletal expansion in Fig. 24 is positive and less than 1.0, which confirms the decrease in void volume which was observed in Fig. 22 and 23 even though the pigment structure was expanding. After the point of maximum expansion, the slope is negative, indicating that the pigment skeleton was being compacted. It should be noted that throughout the region of skeletal compaction, the rate of compaction, as determined by the slope at any point on the experimental curves in Fig. 24, was less for films formed on the porous substrate than for films formed on the nonporous substrate. At the point approaching continuous films where the starch-clay films on the nonporous substrate became denser than those on the porous substrate (see Fig. 22), the compaction of the pigment matrix of the films on the nonporous substrate became great enough such that the matrix actually was more densely packed than that of a film of an equivalent starch content on the porous substrate.

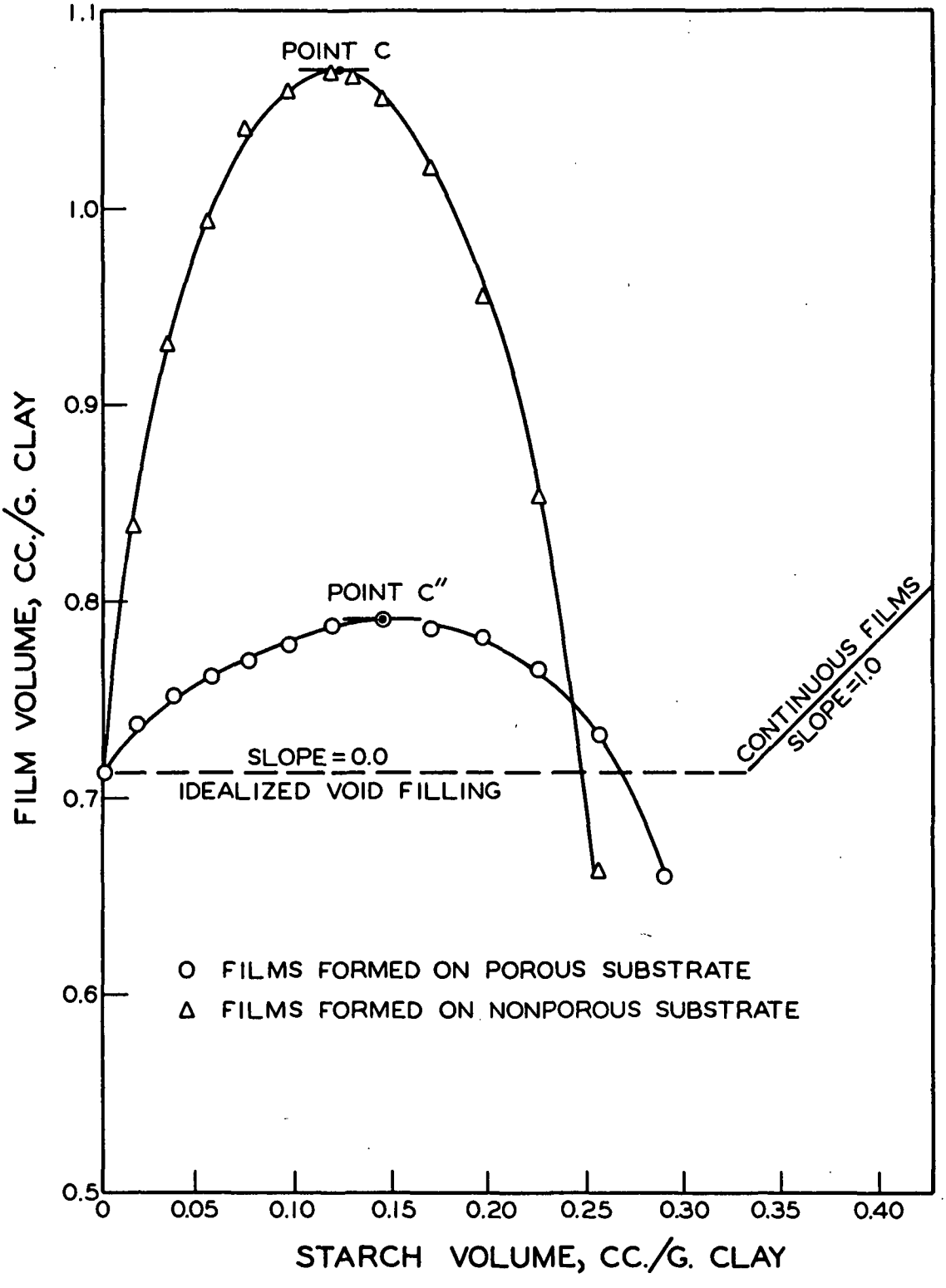


Figure 24. Changes in Film Volume per Gram of Clay with Changes in Starch Volume per Gram of Clay for Starch-Clay Films Formed on a Porous Substrate

Microscopic Examination of Starch-Clay Film Structures

A limited amount of microscopic investigation of coating pore structures was undertaken with the electron microscope to confirm that over most of the porous film region, films formed on the porous substrate exhibited higher densities and lower porosities than films of equivalent starch content formed on the nonporous substrate. Also, it was hoped that some detailed observations concerning pore sizes of films of equivalent starch contents formed on the two substrates might be made. More specifically, it was wondered whether any of the large pores, considerably greater than 0.1 μ in radius, which were observed in films formed on the nonporous substrate, still existed in the films on the porous substrate.

Figure 25 is a cross section of a starch-clay film of $f_p = 0.851$ (starch/clay = 0.1748) formed on a porous substrate. This film is from the region of maximum skeletal expansion (see Fig. 22 and 24) and corresponds quite closely in composition to the film formed on a nonporous substrate which was shown in Fig. 10. It is obvious from comparing the observable pores in Fig. 10 and 25 that the film formed on the porous substrate was much more dense and less porous than the film from the nonporous substrate. Also, it appears in looking at the two cross sections that the very large pores of >1.0 μ in diameter which were present in the film on the nonporous substrate (Fig. 10) do not exist to any extent in the film from the porous substrate. However, many pores can be observed in Fig. 25 which are greater than 0.1 μ in radius.

Two more films formed on the porous substrate, which are roughly of the same starch-to-clay ratio as the films represented in the cross sections shown in Fig. 11 and 12, were examined with the electron microscope. The cross sections of these films are presented in Fig. 26 and 27. Comparison of these cross sections with those of the films of roughly equivalent starch contents from the nonporous substrate again showed that the films from the porous substrate were generally denser and less porous.

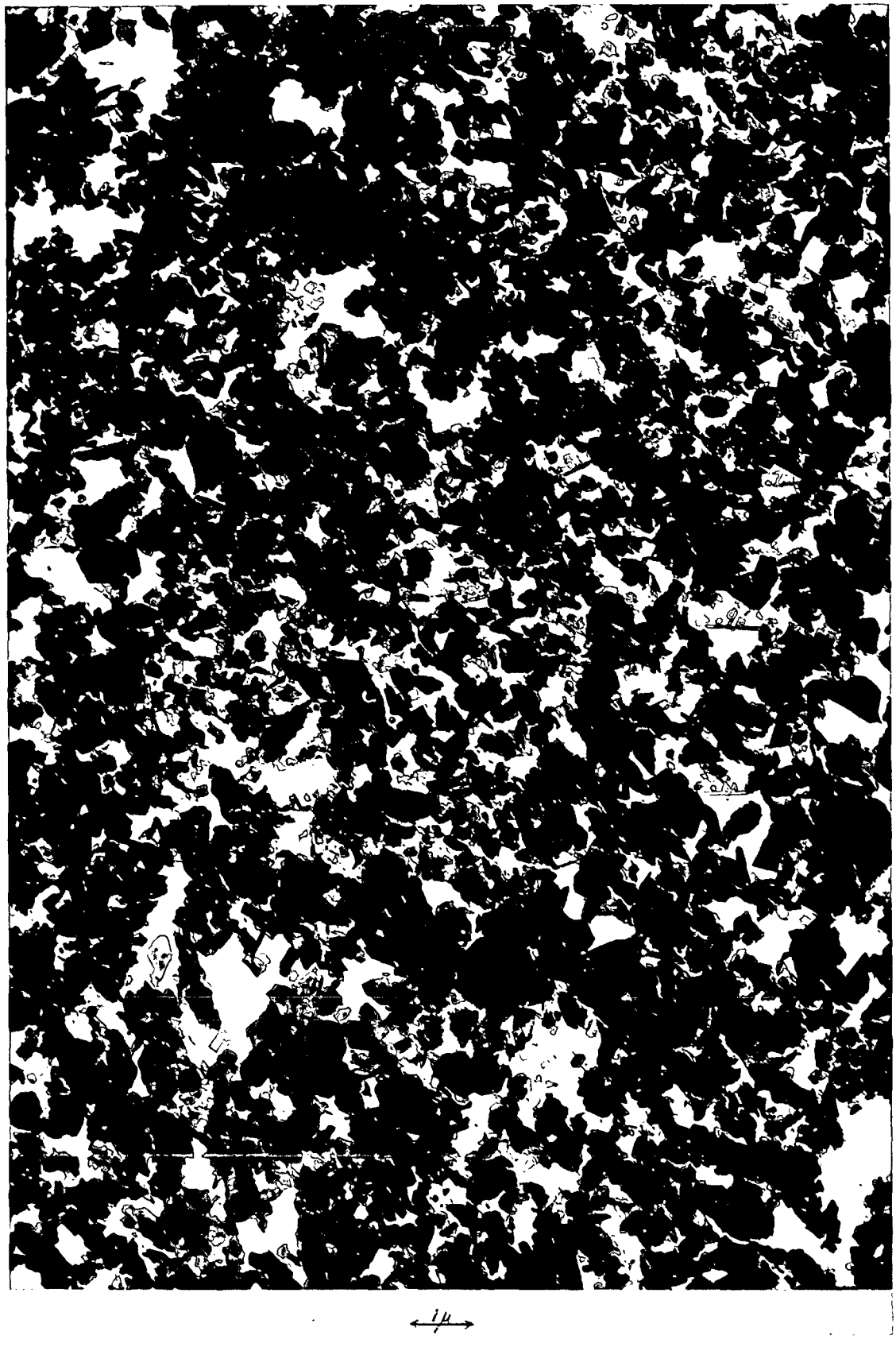


Figure 25. An Electron Micrograph (9000X) of a Cross Section of a Starch-Clay Film of $f_{-p} \approx 0.851$ Formed on a Porous Substrate

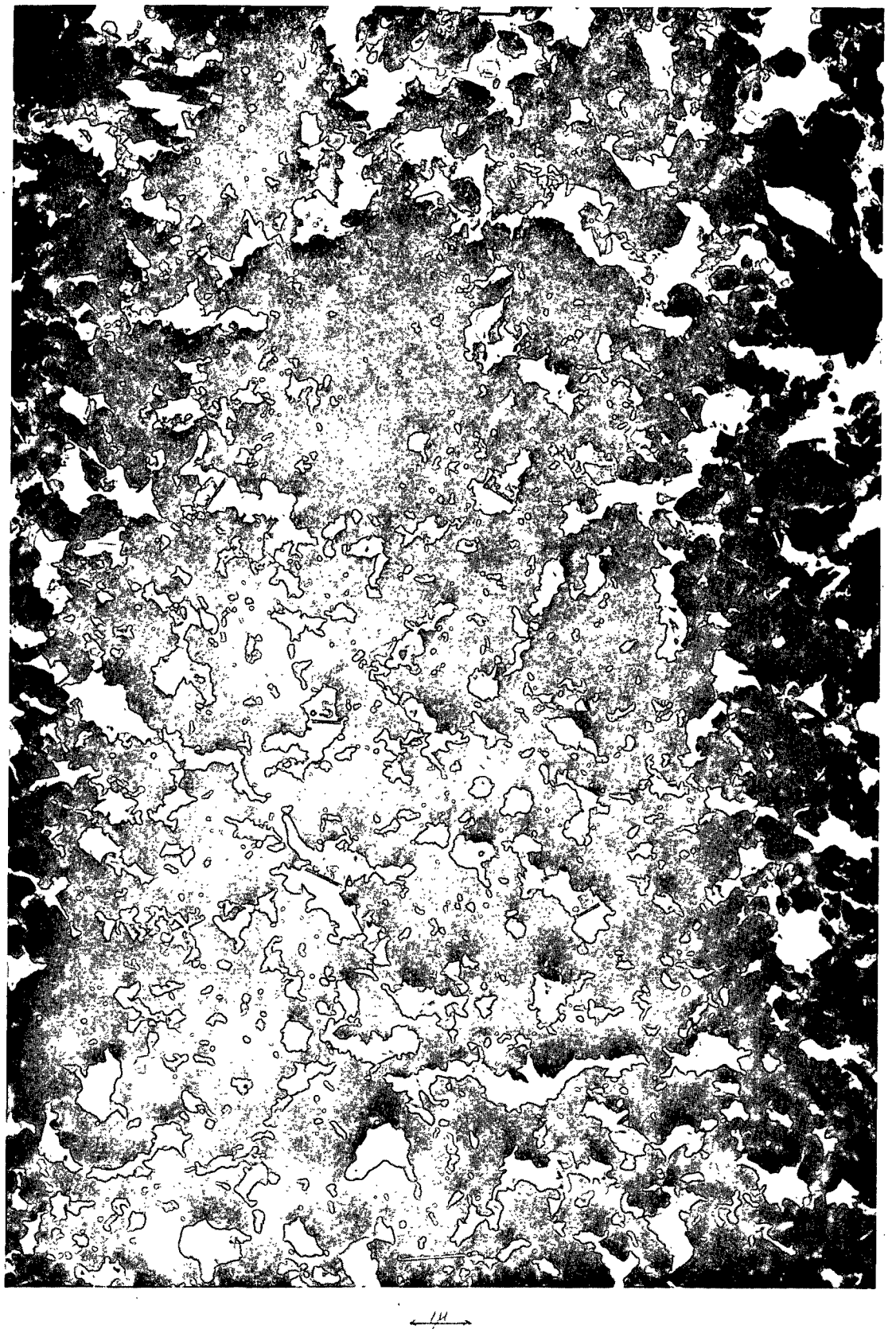


Figure 26. An Electron Micrograph (9000X) of a Cross Section of a Starch-Clay Film of $f_{-p} = 0.829$ Formed on a Porous Substrate

Figure 27. An Electron Micrograph (20,000X) of a Cross Section of a Starch-Clay Film of f_{-p} = 0.745 Formed on a Porous Substrate

Particle Orientation Studies on the Starch-Clay Films

The particle orientations of selected films were determined to ascertain if the expansion and compaction of the pigment skeleton of the films formed on a porous substrate, as shown in the preceding experimental work, caused any measurable changes in the particle orientations among films as was detected for starch-clay films on a nonporous substrate. The particle orientation data obtained are presented in Fig. 28. The data used to determine the particle orientations of each of the films are presented in Appendix V, Tables XVIII and XIX.

The data in Fig. 28 show that the measurable orientations of the films decreased with initial increases in starch from a value of about -3.5 at f_{-p} = 0.934 to a minimum orientation value range of -2.6 to -2.7 which occurred over an f_{-p} of from 0.870 to 0.820. After this minimum orientation region, further increases in starch content produced increases in measurable film orientation up to an observed value of -3.4 at f_{-p} = 0.719. Comparison of these particle orientation results with the interpretations presented for the data in Fig. 22 and 24 showed that decreased particle orientations accompanied skeletal expansion, that the range of minimum orientation corresponded roughly to the region of maximum skeletal expansion, and finally that skeletal compaction was accompanied by increasing particle orientations. The general trend in behavior of the measurable particle orientations of starch-clay films with changes in the pigment skeleton thus appeared to be the same for films formed on both porous and nonporous substrates.

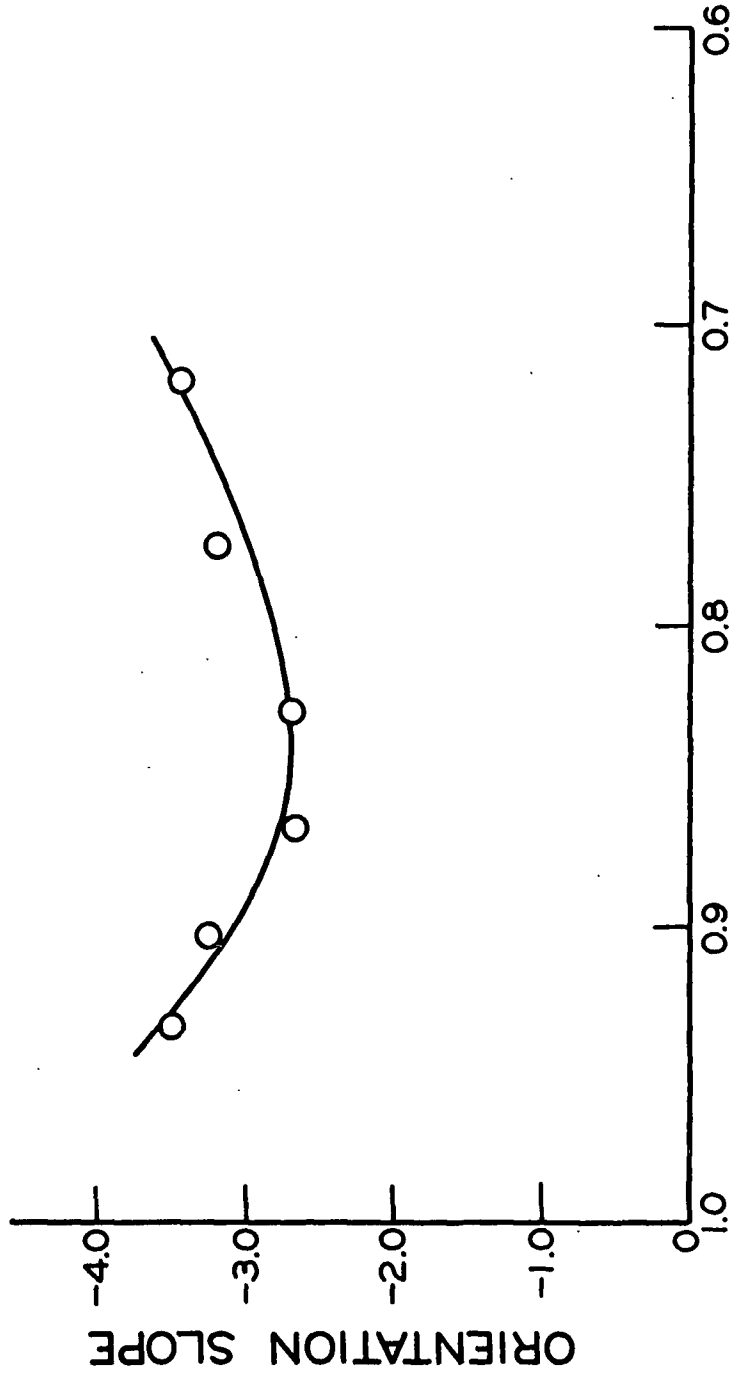


Figure 28. Effect of Changes in Weight Fraction of Pigment, f_p, on Film Particle Orientations of Starch-Clay Films Formed on a Porous Substrate

MECHANISMS BY WHICH THE ADHESIVES STUDIED MAY AFFECT FILM STRUCTURAL FORMATION

The preceding results have shown that none of the three adhesives considered in this study combined with a clay pigment to form a pigment-adhesive film in a manner that could be described by the hypothesis that an adhesive fills the voids in a pigment matrix in an idealized manner. The effect of each adhesive on film structural development has been clearly shown, and the differences among the adhesives in establishing film structures were pointed out. It now seems appropriate to speculate as to the means by which each of the adhesives studied could have influenced the development of coating film structures. The following discussion proposes mechanisms by which each of the adhesives could have affected film structural development in ways which are consistent with the experimental results obtained. A means by which substrate porosity might influence the effect of an adhesive on structural development, as exemplified by the starch-clay system studied, also is presented.

STARCH

It was shown that on a nonporous substrate initial increments of starch caused expansion of the pigment skeleton of starch-clay films which led to increased film void and specific volumes. There are several possible explanations as to how this expansion could have occurred, and most of these explanations are dependent upon the assumption that the phenomenon of starch polymer adsorption onto the clay pigment substrate takes place. Emery (55) and others (56) have discussed the fact that relatively little quantitative work has been done on the important phenomenon of polymer sorption onto a substrate. Even less work has been reported for systems such as the starch-clay one considered here in which hydrogen bonding may occur. However, it has been shown qualitatively in many instances that polymers are adsorbed onto appropriate substrates. La Mer, et al.

(57,58) and others (56,59-62) have shown that various polymers may be adsorbed onto a variety of substrates. Studies on the use of gum polymers as retention aids for paper fillers are based upon the idea that the gums are adsorbed onto pigment surfaces (63,64). Pearl (65) has shown that starch is adsorbed onto fiber substrates. Kohl and Taylor (66) have shown that polymers are sorbed onto and then hydrogen bonded to bentonite clays. La Mer, et al. (58) have shown that starch is adsorbed onto an ore substrate. Michaels (67,68) discusses the adsorption of starch onto kaolin particles, and subsequent hydrogen bonding. Based upon the previous work reported in the literature, the assumption that starch adsorption onto the clay substrate takes place in the system considered here seems quite reasonable.

It seems plausible that the starch is adsorbed onto the clay substrate irreversibly with respect to the water solvent. Also, in a hydrogen bonding system, it seems feasible that once the substrate surface is satisfied with adsorbed starch polymer, the remaining starch might bond with itself more readily than displace polymer already bonded to the substrate. Thus, multilayer adsorption would occur in the system. Pearl (65) showed evidence of multilayer adsorption of amylose starch onto substrates.

Adsorbed starch material on pigment particles would tend to increase the effective particle size of the pigment. These larger encapsulated or coated particles would pack in a less dense manner (3). The packing would be such that the pigment would be separated or wedged by adsorbed or associated starch material, thus causing an expanded pigment structure. Considering the thickness of the layers of adsorbed starch and the magnitude of the increase in effective particle size caused by the adsorbed starch, it seems unlikely that the large structural changes indicated by the data in Fig. 5-6 would occur.

Adsorbed starch polymer may cause expanded and more porous structures in another manner. During the formation of a coating film, a bridging of the pigment particles by the starch polymer may occur. This bridging would prevent the pigment particles from collapsing upon one another as the film is formed, and at a certain point in the drying of a wet film when enough water is evaporated so that a pore structure begins to form, the starch bridges between particles could then begin to spot-weld particles in place. Thus, the particles are never able to collapse as completely upon themselves, and pack as tightly, as when no starch is present.

La Mer (57,58) has shown that polymer materials, including starch, can bridge or flocculate pigment materials causing expanded and more porous pigment-adhesive structures. However, it is doubtful that the bridging which La Mer describes is the same type as that encountered here in the formation of starch-clay films. La Mer found that bridging occurred at very low polymer levels, based upon the weight of the pigment, and proposed that the bridging consisted of a single polymer attached to two pigment particles. Also, the bridging which he observed occurred in dilute systems of pigments and polymers which were never dried to form pigment-adhesive films such as those of this study.

In this study, film expansion and thus bridging continued to quite substantial starch levels. The bridging proposed is by a pigment-starch-starch-pigment mechanism. Michaels (67,68) has mentioned the possibility of this type of bridging occurring. It is felt that bridging of pigment particles by starch, while it may occur in the coating color prior to film application, occurs to the greatest extent as the starch-clay structure is established during drying of the wet film. The relatively slow film formation by mild drying on a nonporous substrate would be conducive to bridging. Adsorbed starch material extending

from two approaching pigment particles would have ample opportunity to associate or bridge as the particles are drawn slowly together. This mechanism of starch bridging, and the resulting expanded pigment structure are illustrated schematically in Fig. 29. The bridging and subsequent spot-welding of pigment particles could cause considerable skeletal expansion and increases in film void volumes with relatively small amounts of starch. The majority of the starch present could still fill voids. Starch bridging which prevents or hinders the packing of the clay platelets in the manner depicted in Fig. 29 is compatible with the decreased measurable particle orientations shown to occur with skeletal expansion.

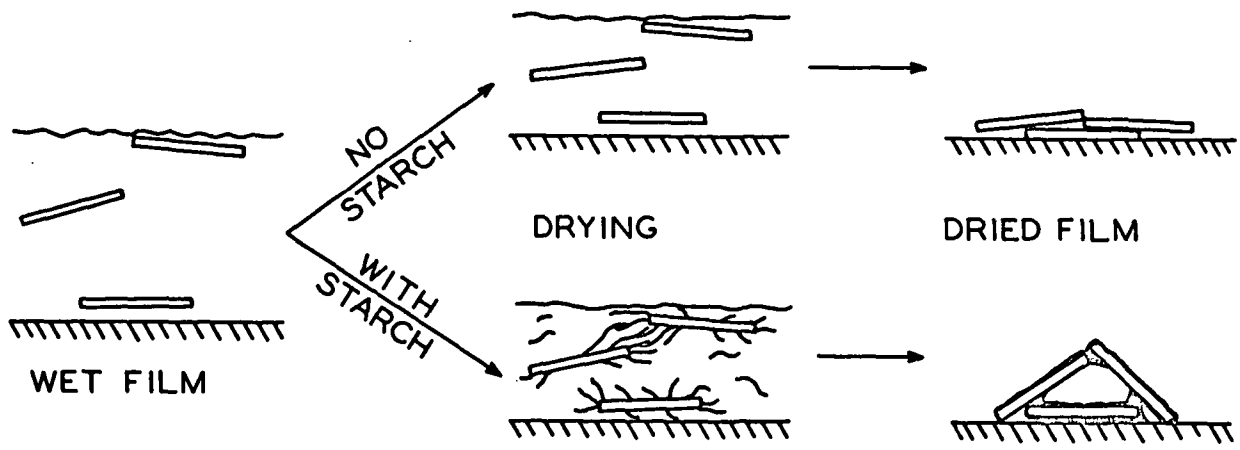


Figure 29. Schematic Representation of Starch Material Bridging Pigment Particles

The expansion of the pigment skeleton of starch-clay films with increasing starch continued at a decreasing rate until a maximum expanded skeleton was reached (Point C, Fig. 5 and 7). Because of the decreasing rate of expansion, film void volumes and specific volumes had reached maximum values, and had begun to decrease before maximum skeletal expansion occurred. The decreasing rate of skeletal expansion with increased volumes of starch, as shown experimentally, may be explained by the fact that although additional starch material is made available for bridging, the time required for film formation may be insufficient for much of the added starch to become involved in the bridging phenomenon.

After the point of maximum film expansion (Point C in Fig. 5), the experimental results showed that the pigment skeleton was collapsed or compacted by additional increases in starch, thus causing rapidly decreasing film void volumes and specific volumes. It may be possible that after the point of maximum structural expansion, a sufficient quantity of starch is present in the coatings to exert a lubricating effect on the pigment particles. There is evidence in the literature that certain polymeric substances might act as lubricants in fibrous systems (69,70), and Mason (71) and Robinson (72) have indicated that this might be true for pigment systems.

In the system considered here, the free starch present in a coating color might reach the point where, during application, particles would tend to slide past one another more readily to give a slightly greater concentration of particles per volume of wet film. This would mean a tighter packing of particles in the final film. At this starch level, there may be enough free or unassociated starch present between particles so that as particles approach one another during the drying of a wet coating film, they tend to slide past one another for tighter packing. This effect could be described as a decrease in starch bridging because enough unassociated starch is present between particles during early drying stages such that bridging is hindered or does not occur as readily. Particles would then have an opportunity to slide together to a greater degree even if they should become bridged and fixed by starch in later drying stages.

Another important factor in film densification could be the compaction of particles by forces arising during the molecular packing of the adhesive. During the later stages of film drying, the adhesive polymers pack together on a molecular level. If sufficient opportunity for movement existed between pigment particles, the alignment of polymer molecules could cause the pigment to be drawn together.

In the case of starch, when a sufficient concentration of starch is present, gelation may occur during drying (31). After the starch level at which maximum structural expansion was reached (see Point C in Fig. 5 and 7), the concentration of starch in the starch-clay films studied here may be great enough for the formation of a starch gel during film drying. This gel may form early enough in drying so that the pigment particles are fixed in position with large amounts of gel between or surrounding them. As drying continues, this hypothesized starch gel should shrink as the starch molecules pack to their final state in the dried film. This shrinkage would exert large forces normal to the substrate, which would tend to align or compact the pigment particles, thus yielding a tightly packed pigment matrix and consequently a dense coating film. A pigment skeleton established in this manner should have the clay platelets aligned more parallel to one another and to the substrate which would cause the increases in measurable particle orientations which were found to accompany structural compaction of the films. The possible lubricating effect of high levels of starch suggested during application and early drying might preferentially align platelets for greater compaction by gel shrinkage.

The starch gel shrinkage suggested here is primarily one dimensional. It is believed that a starch gel would be attached to the foil substrate at many points. Shrinkage in the x-y plane of the substrate would then be restricted, and most of the shrinkage would be in the z-direction.

POLYVINYL ALCOHOL

Initial amounts of PVA are probably adsorbed onto the clay pigment. The probability of polymer adsorption onto a substrate and the conditions necessary for adsorption were discussed in connection with the starch system, and the same principles should apply to PVA adsorption. The adsorbed PVA may increase the effective particle size of the pigment, thus causing it to pack less compactly.

The PVA also may wedge particles apart at points of contact in the final film. These things would contribute to the expanded, more porous pigment skeleton which was shown to occur in PVA-clay films with initial increases in PVA. However, considering the amount of PVA which is present in films where skeletal expansion occurred (see Fig. 14 and 16), it seems reasonable that these effects would be minor.

As in the starch-clay system, the major cause for expanded pigment structures and subsequent increases in film void volumes and specific volumes with increases in PVA probably is the bridging of pigment particles by the polymer. The experimental results indicate that the mechanism by which bridging occurs may be different for PVA than it was for starch. Structural expansion, and thus bridging of starch-clay films, continued up to a relatively high adhesive-to-pigment ratio. This was felt to be due to the nature of the starch adhesive and its ability to associate with itself, thus forming complicated pigment-starch-starch-pigment bridges. PVA does not tend to associate or bond with itself readily in solution, as exemplified by the fact that PVA solutions are stable over long periods of time, and thus the bridging of two pigment particles by the association or combining of PVA material extending from each of two approaching particles, as was the case for starch, is doubtful.

For PVA, the proposed bridging may more nearly approach that type discussed by La Mer (57,58). The long-chain PVA molecules may be adsorbed onto pigment particles at many points along the chain. If the surface area of the pigment is great enough, or the concentration of the PVA low enough, a PVA polymer may be adsorbed onto two pigment particles. These particles are then bridged, and if this behavior extends throughout a PVA-clay system, the result is ultimately an expanded pigment structure in the final coating film. The bridging could take place in the coating color and should be encouraged further during the process of film formation.

As the PVA level is increased, bridging should increase until enough PVA is present so that the surface sites on pigment particles can be satisfied without bridging. At this point, because the PVA does not tend to associate with itself, bridging should begin to decrease. One can estimate roughly from the surface area of the clay [determined to be 14.01 $M^2/g.$ by Kraske (3) for his 0.5 to 1.0 μ clay fraction of a similar particle size distribution to that used in this study] and the density and approximate molecular thickness of a PVA molecule that in this study about 1 part PVA per 100 parts clay could satisfy all bridging sites if perfect adsorption took place. Based on La Mer's studies, optimum bridging then would occur at 0.5 part PVA per 100 parts clay. The point of maximum film expansion detected in this study occurred at about 2 or less parts of PVA per 100 parts pigment. Maximum structural expansion should correspond to maximum bridging. When one considers that all of the PVA probably may not have the opportunity to adsorb, this figure is not unreasonable for a maximum bridging effect.

The possibility exists that a film of greater skeletal expansion exists for the PVA-clay system than was detected in this study. The results indicated that the skeleton probably would not be expanded to a much greater degree, but that the maximum expansion could occur at a significantly lower PVA level. As has been pointed out, if La Mer's hypothesis of flocculation is correct and if it applies to the PVA-clay system considered here, maximum bridging would occur at the point where 50% of the pigment surface was covered with PVA, or at 0.5 part PVA per 100 parts clay.

The type of bridging proposed for the PVA-clay system would help explain the initially rapid skeletal compaction after the maximum expansion. Further increases in PVA would decrease bridging by tying up available sites. With a reduction in bridging, the pigment particles would tend immediately to pack together in a tighter manner and the internal void volumes of films quickly would

be decreased. As the level of PVA present in colors increases, the PVA may begin to exhibit lubricating properties similar to those discussed for the starch, and the compaction of the skeleton by the molecular packing of the PVA molecules should become important.

The compaction of the pigment skeleton of starch-clay films at higher starch levels was attributed largely to the forces developed during the shrinkage of a starch gel. This was accompanied by an increase in the degree of platelet orientation parallel to the substrate. Molecular packing of the PVA adhesive probably is important in the compaction of the pigment skeleton of PVA-clay films. This is emphasized by the fact that films just prior to the continuous region were more dense than could ever be predicted by idealized void filling of a pigment film. However, no significant increase in platelet alignment parallel to the substrate was detected.

In the drying of a PVA-clay system, the liquid phase should remain fluid throughout almost the entire period of film formation. The PVA solution present concentrates, but no adhesive network structure such as that visualized in a starch gel occurs. The clay platelets would be forced together during drying until a pigment matrix is formed throughout which is a fluid, concentrated, PVA solution. As drying continues, the pigment skeleton could be compacted first by surface tension forces, and finally by the alignment of the PVA polymer molecules. Since the PVA solution remains fluid during drying, the forces acting on the pigment particles are three dimensional, and no preferred compaction of the pigment matrix, as may occur with the shrinkage of a starch gel in the z-direction, takes place. Densification of a film may be enhanced by the compaction of localized pockets of pigment platelets by molecular packing of the PVA molecules, but while the pigment particles may be aligned or compacted parallel to one another in the localized pockets, these pockets need not be aligned parallel to the substrate. Thus, the measurable orientation of the PVA-clay films need not increase.

LATEX

The deviation of the latex-clay films with increasing latex from idealized adhesive void filling may be explained by the nature of the latex adhesive. The term latex refers to colloidal suspensions of polymers as prepared by emulsion or suspension polymerization (73). The method of preparing the styrene-butadiene latex used in this study was such that the copolymer particles were stabilized principally with a nonionic system (74). The emulsifying detergent used provided a protective colloid effect around the copolymer particles in the final emulsion.

When an emulsion latex, such as the one used here, is used as a coating pigment binder, the coating color consists of two colloidal substances, the pigment particles and innumerable discrete semisolid particles of polymer (75). The polymer particles are slightly negatively charged and have little affinity for the negative pigment particles with which they are intermingled. Also, because of the protective colloid action of the emulsifying detergent, the polymer particles never come in close enough proximity to pigment particles for any sorption of polymer to take place.

When a coating color system like the one which has been described is applied to a substrate, nothing more than a layer of a suspension of two independent types of colloidal particles is present. At this point, the system is analogous to applying a suspension of two different pigments to a substrate. With the removal of the aqueous external phase that occurs on film drying, the dispersed pigment and polymer particles are crowded closer and closer together until long before all the water has evaporated their peripheries begin to touch. Further drying leads to a deformation of the polymer droplets which assume polyhedral shapes, thus increasing their mutual areas of contact (75). At first, coalescence is inhibited by the adsorbed layers of stabilizers and dispersants, which also prevent the polymer from wetting the pigment. Gradually however, film formation commences by the merging of polymer particles and their attachment to the pigment.

Based upon the picture presented for film development in a latex-clay system, no interaction, such as sorption, occurs between the latex and clay particles during film formation. The clay pigment packs independently of the latex, except where mechanical interaction between the two different particles takes place.

The expansion of the pigment skeleton of latex-clay films with increasing latex content, and the resulting divergence from idealized void filling as shown in Fig. 18, is probably caused by latex particles physically wedging clay particles apart. While the latex may tend to fit between clay platelets and fill pores, its particle size is such that it creates more interpigment space between pigment particles. The average particle size of the latex used in this study was 0.2 μ. Comparing this to the size of the clay platelets present, which was from 0.5 to 1.0 μ e.s.d., and visualizing what the size of the internal pores of these packed platelets might be in a pigment film, it seems unlikely that latex bound films could be formed with constant pigment packing. Even with deformation of latex particles upon final film drying, the clay platelets would certainly still be wedged apart. Referring to Fig. 18, at low latex levels a close proximity to idealized void filling was apparent, but as more latex particles were available for greater mechanical interaction, the pigment skeleton steadily expanded and the divergence from void filling increased until a continuous film was reached.

The experimental results showed that after an assumed initial disruption of platelet orientation by the latex, film particle orientation then increased with increasing latex despite continued expansion of the pigment skeleton. What may happen is that after the platelets are disrupted by the initial addition of latex particles, further increases in latex have a leveling effect which leads to increased orientation. This is comparable to leveling a simple beam by supporting it at more points along its length. The principle is illustrated in Fig. 30.

Figure 30. Effect of Latex Particles on the Packing of Clay Platelets

It was mentioned in the discussion of the experimental results that a situation might exist where a latex-pigment system might approach a condition of idealized void filling very closely. If sufficiently small latex particles with respect to appropriately large pigment particles were used to form latex-pigment films, the latex particles, at least at lower latex-to-pigment ratios, might actually fit between the packing pigment particles without significantly affecting the alignment of the pigment skeleton. This would be a very specific exception to the general behavior noted for the latex-pigment system studied here.

SUBSTRATE POROSITY

It was shown experimentally in this study that the starch adhesive had a very pronounced effect upon the structural development of starch-clay films, and a mechanism for explaining this effect was proposed for films formed on a nonporous substrate. Later, it was shown experimentally that the porosity of the substrate upon which starch-clay films were formed had a significant influence upon the degree to which film structure was affected by the starch. The purpose of the following discussion is to present a means by which substrate porosity may affect the mechanism which was suggested earlier to explain the starch adhesive's influence on starch-clay structures.

When a coating color is applied to a porous substrate, migration of the liquid phase (vehicle and some starch) into the substrate occurs. This migration has been shown by many investigators (24,26,76-78). The rate of liquid migration into an idealized pore system has been described by Washburn (79).

Migration of the liquid phase causes fluid drag forces to be established in the wet coating film. These forces cause the pigment particles to be drawn toward the substrate, thus rapidly establishing a pigment skeleton or matrix. The concept of film formation during later stages is the same as that pictured for a system on a nonporous substrate.

The rapid formation of a pigment skeleton in a film applied to a porous substrate greatly reduces the opportunity for the starch present to bridge approaching pigment particles. The bridging which still occurs would never approach the complexity or magnitude of that found in the films on a nonporous substrate, where ample time was available for the development of starch bridging. The skeletal expansion which was interpreted from the results in Fig. 22 and 24 is due to whatever bridging still may occur, and to the wedging apart of pigment particles at points of contact by volumes of starch.

The data for the films on the porous substrate showed that the pigment skeleton went through a maximum expansion and was then compacted with further increases in starch content. Significantly, maximum skeletal expansion occurred at approximately the same starch content for films on both porous and nonporous substrates. It appears that if a certain critical starch concentration exists in the wet coating film, then, regardless of the substrate to which it has been applied, a possible lubricating effect followed by the formation and subsequent shrinkage of a starch gel network occurs, and the pigment skeleton is compacted. Because the formation of the pigment matrix of films on a porous substrate is affected by flow forces, the degree of skeletal compaction is less than for films of equivalent starch levels on the nonporous substrate. The pigment skeleton is fairly well defined prior to gelation of the starch during drying, and shrinkage of the gel during later drying stages cannot compact the pigment particles together to the same degree as occurred on the nonporous substrate.

The possibility should not be overlooked that decreases in the rate of penetration of the liquid phase of a color into the porous substrate with increases in starch may affect film structural formation. The rate of penetration is inversely proportional to the square root of the viscosity of the liquid phase (79), and this viscosity should increase with increased starch. A decrease in the rate of penetration would reduce the flow of fluid surrounding the pigment particles in the wet film. This would reduce the rate of skeletal formation and would enhance film bridging and expansion up to certain starch levels. Then, after the experimental point of maximum expansion (Point C" in Fig. 22 and 24), a decreased rate of penetration would continue to cause a decreased rate of formation, allowing lubrication, gelation, and subsequent gel shrinkage to play more important roles in structural development.

Throughout the preceding comparisons of the starch-clay film system on porous and nonporous substrates, the effect of a migrated quantity of starch was neglected. If the quantity of starch lost from a color contributed significantly to the differences in structure, then perhaps films should be compared on the basis of original starch color contents. One can easily show that the structures of films on the two substrates differ by more than just starch volumes. The films formed on foil have the same composition as the original coating color. If one considers a point on the nonporous substrate curve (see Fig. 22), and assumes no structural change takes place other than the loss of a certain volume of starch when the same film is applied to a porous substrate, then a film of higher specific volume must result. Graphically, this means that the point on the nonporous curve must be connected to some point on the porous curve by a line with a slope equal to or greater than 0. Obviously, for films of a weight fraction of pigment greater than 0.78, this is impossible. Differences in the pigment skeleton must be present between films formed from the same color on the two substrates.

The remote possibility exists that the quantity of starch lost to the substrate might decrease the material available which contributes to bridging, and thus expansion of the pigment skeleton. However, Dappen (78) has shown that roughly only 4-5% of the coating color starch is lost through migration, and rough calculations made from the results of this study indicate that a maximum of about 6% could migrate into the substrate. Thus, considering the amount of starch which remains in the color, and considering that only a portion of the total available starch becomes involved in bridging (the majority of the starch fills interpigment spaces), it seems highly unlikely that the small quantity of migrated starch could seriously affect the amount of starch available for bridging.

It is concluded that the quantity of starch that migrates into a substrate during film formation has little effect upon film structural development. Instead, it is hypothesized that the manner of structural establishment is important. The forces caused by the migration of liquid into the substrate tend to form film structures in a manner so as to damp the effect of the starch.

One possibly significant but undetectable difference between the starch-clay films formed on the porous and nonporous substrates should be pointed out. The films in this study were compared on the basis of average film physical characteristics; that is, the physical characteristics determined for the films were averages over an entire film thickness. Obviously, variations in these physical characteristics could occur to some extent over the thickness of a film, and such variations are not discernible from the data obtained in this study. For two films of equivalent total starch content, one formed on a porous substrate and the other on a nonporous substrate, the distribution of the starch over the film thicknesses could differ considerably between the two. For example, one might suspect that a film formed on a porous substrate would have a less uniform

distribution of starch within its pigment matrix, due to migrational forces, than a film of equivalent starch content formed on a nonporous substrate. Thus, significant changes in the differences in film composition and physical characteristics between films could occur over film thicknesses, but as pointed out, only the average differences are compared in this study.

SPECULATIONS CONCERNING THE BEHAVIOR OF PVA-CLAY AND LATEX-CLAY FILMS ON A POROUS SUBSTRATE

Although no experimental data were obtained for the PVA- and latex-bound coating films on a porous substrate, some speculatory remarks as to what their behavior might be can be made. Considering the similarities of starch- and PVA-bound films on a nonporous substrate, it is expected that the effect of the PVA in structural formation would be reduced on a porous substrate. The forces arising by liquid-phase migration into the substrate would become a factor in the establishment of the pigment skeleton. However, because of the proposed difference in the bridging of pigment particles by starch and PVA, the effect of the PVA in structural formation may not be reduced to the same degree as was the effect of the starch. It is anticipated that sufficient bridging still would occur in the PVA-clay system such that the degree of maximum skeletal expansion would be great enough to continue to cause maxima in film specific volumes and void volumes.

A latex-bound film system should show essentially the same behavior on a porous substrate as it did on a nonporous substrate. The relationship proposed between a latex and a clay pigment is such that an increased rate of film formation should have little effect on final film structure.

In general, the effect of substrate porosity would be to reduce the role of adhesives similar to starch and PVA in film structural formation. These adhesives are sorbed onto and subsequently bridge particles during film formation. Flow forces caused by migration of some of the color would tend to compete with or damp the effect of such adhesives on structure. Substrate porosity would not influence significantly the role of nonadsorbing adhesives, like a latex, in film structural formation.

A DISCUSSION OF SOME OF THE WORK ON COATING PRESENTED IN THE LITERATURE IN LIGHT OF THE RESULTS OF THIS STUDY

It would be impossible to discuss all of the coating literature which might be pertinent to this study. Furthermore, it was not the purpose of this thesis to explain coating end-use properties in terms of the results obtained. However, in order to emphasize the contribution of this study toward a better understanding of pigment coating, a brief discussion of some of the coating literature as related to the results obtained here seems appropriate.

The previous approach taken by some coating researchers, such as Cobb (8) and Hagemeyer (10,11), that a study of the packing characteristics of pigment particles alone can lead to a complete understanding of coating film structural formation is in error. The results of this study have shown that a pigment does not pack independently of the presence of an adhesive, and that an adhesive does not exhibit idealized void filling of a pigment matrix in the formation of pigment-adhesive coating films, as was assumed by Cobb and implied by Hagemeyer in their studies. Future study on film structural development and subsequent film properties must consider the effect of the adhesive on the establishment of coating film structures.

The more recent methods developed by paint investigators (18,19) for determining the C.P.V.C. of pigment-adhesive films, have been based upon the assumption that idealized void filling describes the relationship of the pigment and the adhesive for films with pigment levels above the C.P.V.C. These methods have been applied mostly to latex-pigment films, and as was indicated in a previous discussion, the possibility exists that a unique combination of latex and pigment particle sizes could be used to form films where the concept of idealized void filling might be very nearly valid. However, the work here indicates that generally

in a latex-clay system idealized adhesive void filling over the porous film region does not occur, and thus these methods developed for determining the C.P.V.C. of films are of very questionable value.

In comparing the end-use properties of coating films formed using different adhesive binders, it has become rather common to attribute differences in film properties to differences in adhesive volumes. Colgan and Latimer (13) and Beeman and Beardwood (14) in comparing films using starch and PVA as binders do this. Again, the implied assumption is always that the same interpigment space is available to be filled by an adhesive. The results of this study have shown that these two adhesives form different structures in combination with the same clay pigment, and that comparisons based upon a common pigment skeleton are not valid. Therefore, at some equivalent standard, such as film strength or weight of adhesive, properties such as opacity or ink receptivity cannot be explained solely in terms of differences in adhesive volumes.

In some cases, studies on coating film properties, such as that of Robinson and Linke (12) on coating film opacity, have been based upon the improper assumption of idealized void filling and yet appear to have yielded satisfactory correlations between coating variables. In view of this thesis study, it is concluded that such apparent correlations are fortuitous and that they have developed due to offsetting effects of other bogus assumptions or through experimental error.

The preceding discussion has pointed out some of the previous work in the literature which has been based upon the invalid concept of idealized adhesive void filling, and is thus at least partially incorrect. It is hoped that the results obtained in this study also might be of value in interpreting, and hence making more useful, some of the better work in the area of coatings. For example,

some of the conclusions reached in this study have direct applicability to the work done by Eames (4) on the strength development of coating films.

In his study, Eames (4) has taken perhaps the most fundamental approach to the measurement of coating film strength that is reported anywhere in the literature. Eames suggested that a dense coating film was not necessarily a strong film. He implied that dense coatings of a high degree of platelet orientation might have zones of adhesive depletion which failed under his transverse tensile test. However, he showed definitely that coating films formed on Millipore filter paper were stronger at equivalent starch levels than those formed on a nonporous substrate. The results of this study show that the films on a nonporous substrate are much less dense than those on porous Millipore over the starch range in which Eames worked. Eames's conclusion that denser films are weaker does not seem valid. Instead, it appears that the denser films would be the stronger.

Eames extended his hypothesis concerning film densities and strengths to films formed on substrates of varying porosity. He showed experimentally that film strength tended to increase with increased substrate porosity. He also reported that film density decreased with substrate porosity, and thus the less dense films were stronger. The method which he used to determine film densities was the mercury pycnometer technique that has been described earlier in this work as unsatisfactory. The results of this study have shown that increased substrate porosity would tend to densify films. The conclusion, again, is that denser films would have greater bonding and greater strength.

Finally, Eames suggests that his transverse tensile strength of starch-clay coatings is governed by the final adhesive distribution in the coating. He states that the distribution of voids and the degree of particle orientation within the pigment matrix may affect strength through their effects on the adhesive distribution.

It has been shown in this study that the adhesive itself significantly affects the establishment of the pigment matrix and thus interpigment space and particle orientation. Therefore, coating strength might be thought of as a complex function of the effect of the adhesive upon pigment matrix formation, and its subsequent distribution within the matrix which it has helped establish.

SUMMARY AND CONCLUSIONS

SUMMARY OF EXPERIMENTAL WORK

The role of the adhesive in coating film structural development was investigated. The simplifying hypothesis used by previous workers of idealized adhesive void filling was found to be invalid. Adhesives did not fill voids, but interacted with a pigment in a much more complex manner. This was shown for three widely differing adhesives — a starch, a polyvinyl alcohol, and a latex — and for films formed on both porous and nonporous substrates.

Different adhesives combined with the same pigment to form significantly different pigment-adhesive structures. Mechanisms were proposed to explain how each of the three adhesives studied could have combined uniquely with the same clay pigment to develop very different film structures. It is expected that coating films using different starch binders and formed under the conditions specified in this study would exhibit similar, although perhaps not identical, behavior to that observed here. The same would be true for other polyvinyl alcohols or latices. Thus, the behavior of the adhesives studied should be representative of other adhesives of the same type. Also, based on the explanations presented here, coating adhesives may be grouped loosely as adsorbing and nonadsorbing. Distinct differences in film structural development should be expected when adsorbing and nonadsorbing adhesives are compared.

The substrate had a pronounced effect on the formation of a pigment-adhesive structure in the one coating system studied here. For the substrates considered, the porous substrate influenced the development of film structure in such a manner as to reduce the effect of the adhesive in structural formation. The porous substrate tended to force the adhesive to approach a condition of idealized void filling. However, the deviation from idealized void filling was still very significant.

In the course of meeting the objectives of this thesis, some experimental contributions were made. A technique was developed for measuring the density of coating films. With proper care, this technique is applicable to all coating films including very fragile films of low adhesive levels. Also, a method of examining pigment-adhesive films formed on a nonporous substrate was developed. Films formed on nonporous tinfoil could be isolated readily for study.

The experimental techniques developed by Kraske in his thesis work were applied for the first time in a detailed coating study. Clay platelet orientation as determined by x-ray diffraction was used with qualitative success to help describe and explain film structural changes. Gas adsorption techniques, while limited in usefulness in this study, provided corroborating structural information.

An examination was made of coating cross sections utilizing the electron microscope. The electron micrographs obtained represented an improvement over previous attempts at examinations of this type reported in the literature. The cross-sectional views were useful in visually confirming the presence of pores of particular sizes.

In the introductory remarks to this work, the importance of film structure in relation to coating end-use properties was emphasized. On the basis of the results of this study, a brief discussion was presented on some of the previous coating work presented in the literature. Discussions of the properties of coatings which implied that adhesives merely filled voids were pointed out as being unsatisfactory.

CONCLUSIONS

The following conclusions are derived from the results of this study:

1. The simplifying assumption of idealized adhesive void filling for

coating films is not valid. The relationship between the adhesive and pigment is much more complex.

2. Different adhesives may combine uniquely with the same pigment to yield different pigment-adhesive structures.

3. The substrate has a significant effect on film structural development. For the system considered in this study, increased substrate porosity tended to damp or decrease the influence of the adhesive in establishing film structure.

SUGGESTIONS FOR FUTURE WORK

The following suggestions for possible future investigations related to the formation of pigment coating structures have evolved during the course of this thesis study:

1. A study to determine the mechanisms by which adhesives may interact with pigments during the establishment of pigment-adhesive film structures might be undertaken. In the course of this study, mechanisms were proposed for pigment-adhesive interactions which were consistent with the observed effects of the adhesives on the formation of pigment-adhesive film structures. However, these hypothesized mechanisms have not been verified experimentally.

2. A complete study of the influence of substrate porosity upon the effect of adhesives on film structural development is needed. The results obtained in this study definitely established that the porosity of the substrate affects the development of coating film structures, but there is much work to be done on how changes in substrate porosity would influence the formation of films from a particular pigment-adhesive system, and whether changes in substrate porosity would affect film formation in one pigment-adhesive system more than another.

3. Finally, the influence of changes in the important variable of drying rate upon the effect of the adhesive on film structural formation was not considered in this study. Much work is needed in this general area.

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APPENDIX I
ADDITIONAL INFORMATION ON EXPERIMENTAL PROCEDURES

TABLE III

REPRODUCIBILITY OF DENSITY DETERMINATIONS ON COATING FILM SAMPLES

Sample	Pigment Weight Fraction, f_p	Clay Wt., g.	PVA Wt., g.	PVA/Clay	Film Area, $cm.^2$	Film Thickness, μ	Density, g./cc.	Film Sp. Volume, v_f, cc./g.
1	0.9265	0.01387	0.0010	0.0793	3.646	31.51	1.263	0.7918
2	0.9260	0.01252	0.00100	0.0793	3.512	30.34	1.269	0.7880
3	0.9260	0.01202	0.00097	0.0793	3.397	30.18	1.266	0.7899
4	0.9262	0.01206	0.00096	0.0793	3.366	30.67	1.260	0.7936
5	0.9260	0.01202	0.00096	0.0793	3.408	30.11	1.265	0.7905
6	0.9261	0.01178	0.00094	0.0793	3.438	29.24	1.265	0.7905
7	0.9261	0.01104	0.00088	0.0793	3.346	28.21	1.262	0.7923

NOTE: Samples 1 through 5 were from different positions within the same coating film. Samples 6 and 7 were from two separate coating films which were applied from the same coating color as the film from which the first five samples were taken.

TABLE IV

DENSITIES OF ADHESIVE FILMS

Adhesive	Film Density, g./cc.
Clinton 632 Starch	1.480
Du Pont 71-30 PVA	1.267
Dow Latex 512R	1.0109

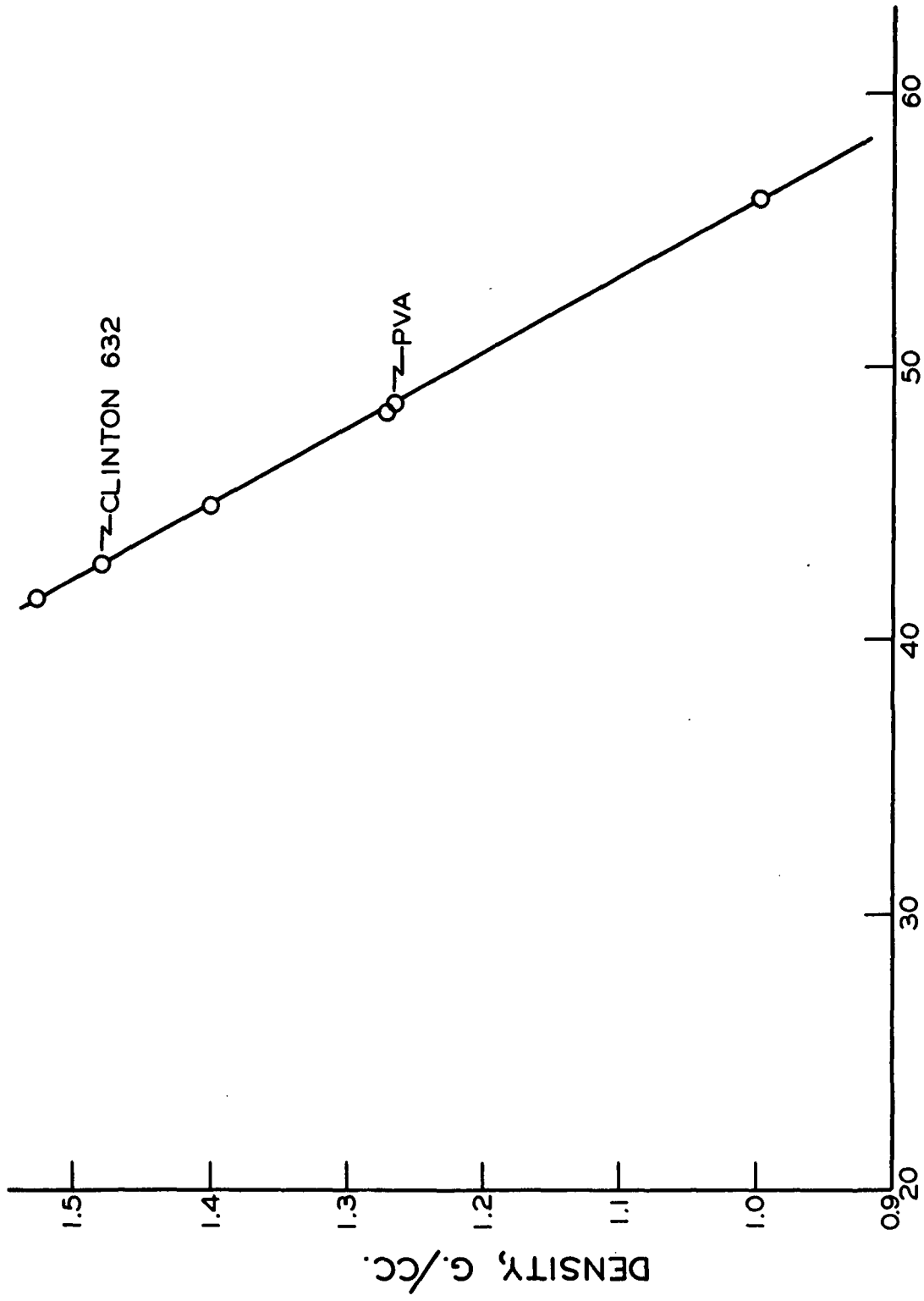

Figure 31. Determination of Densities of Starch and PVA Adhesives

DETERMINATION OF AVERAGE PARTICLE ORIENTATIONS OF COATING FILMS BY X-RAY DIFFRACTION

DERIVATION OF THE EQUATION FOR THE CALCULATION OF RELATIVE INTENSITIES

When a clay coating sample is tilted in an x-ray beam to an angle, α, as illustrated in Fig. 32, the path length of the x-rays in the specimen changes. It is necessary to correct for differences in adsorption of the diffracted beam caused by these changes in path length before the measured intensities at various values of α can be compared with the value obtained at $\alpha = 0$ to obtain relative intensity values.

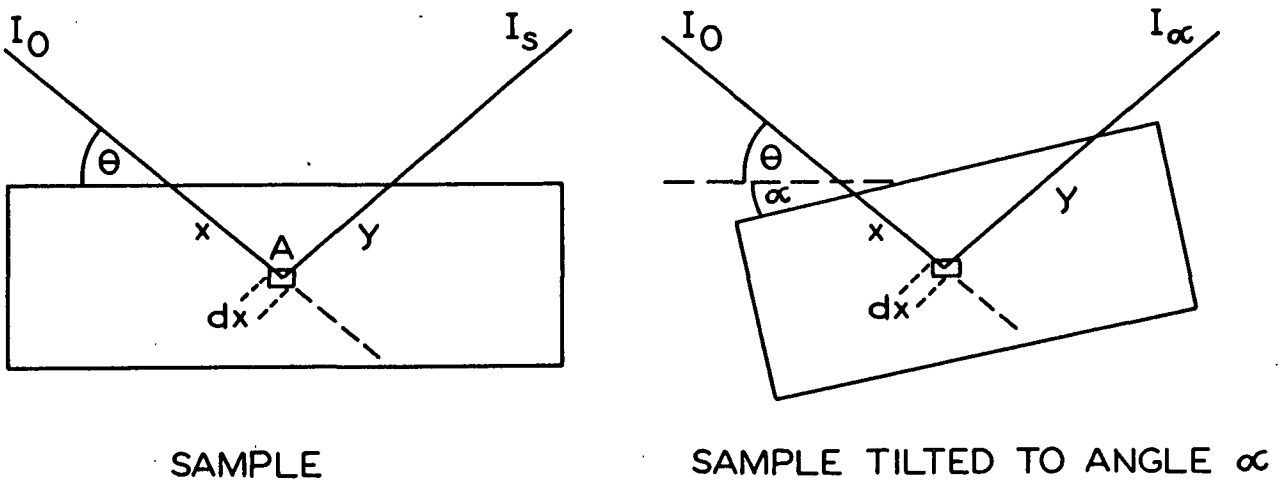

Figure 32. X-Ray Path in Infinitely Thick Samples

Considering the samples shown in Fig. 32 to be infinitely thick to x-rays, Field and Merchant (38) have presented the following derivation of the required adsorption correction factor.

I_o = incident x-ray intensity,

x = the distance along the incident x-ray path from the surface to an increment of thickness (dx) at Point A,

I_a = the x-ray intensity at Point A,

dx = an increment of thickness along Path X,

D = the fraction of x-rays scattered per unit thickness of the sample,

y = the path length of the diffracted beam in the sample,

I_s = the intensity of the diffracted beam leaving the specimen in the normal ($\alpha = 0$) position,

I_α = the intensity of the diffracted beam leaving the sample when it is tilted at some angle,

μ = the linear absorption coefficient of the specimen, and

θ = convenient Bragg angle for the specimen.

Considering the sample tilted at angle α, the x-ray intensity reaching Point A is

$$I_a = I_o e^{-\mu x} \qquad (1).$$

The incident beam in passing through the increment of thickness (dx) along the path x at Point A, contributes a minute fraction (D) of its energy to the diffracted beam. At Point A:

$$dI_\alpha = I_a D dx = I_o e^{-\mu x} D dx \qquad (2).$$

This portion of the beam which is diffracted at Point A loses some of its energy in traversing the path y from Point A to the surface of the specimen.

$$dI_\alpha \text{ (at the surface)} = (I_o e^{-\mu x} D dx) e^{-\mu y} \qquad (3).$$

Equation (3) may be simplified by using the relationship:

$$y = x \sin(\theta + \alpha)/\sin(\theta - \alpha)$$

and defining $y = xM$, where $M = \sin(\theta + \alpha)/\sin(\theta - \alpha)$. Then,

$$dI_\alpha \text{ (at surface)} = I_o D e^{-\mu x} e^{-\mu x M} dx \qquad (4).$$

If it is assumed that dx is essentially zero in thickness, it is possible to collect terms and integrate Equation (4). Since the specimen is infinitely thick to x-rays, the integration is from $x = 0$ to $x = \infty$.

$$I_\alpha = I_o D \int_o^\infty e^{-(1+M)\mu x} dx \qquad (5);$$

thus,

$$I_\alpha = I_o D/\mu(1 + M) \qquad (6).$$

When $\alpha = 0$, or the sample is not tilted, $M = 1$, so that

$$I_{\alpha=0} = I_s = I_o D/2\mu \qquad (7).$$

From Equations (6) and (7), the following ratio may be formed:

$$\frac{I_\alpha}{I_s} = \frac{2}{(1 + M)} \qquad (8).$$

Equation (8) is the ratio of intensities due to absorption differences alone. Experimentally measured intensities at finite values of α can be divided by $2/(1 + M)$. This yields an intensity value which has been corrected for absorption differences due to tilting the sample, and this value can be compared directly to the diffracted intensity at $\alpha = 0$ to obtain the relative intensity.

Equation (8) is derived for specimens infinitely thick to x-rays. The coating samples, even as 4-ply composites, used in this study were not sufficiently thick so as to approximate infinite thickness to x-rays. Kraske (3) modified the Field and Merchant derivation to apply to thin films. For a thin film, it is necessary to integrate Equation (5) from $x = 0$ to $x = x$.

$$I_\alpha = I_o D \int_o^x e^{-(1+M)\mu x} dx \tag{9}$$

and

$$I_\alpha = \frac{I_o D}{\mu(1 + M)} [1 - e^{-(1+M)\mu x}] \tag{10}.$$

In the case of a thick film, the incident x-ray beam path length is constant regardless of the angle of α. However, for a thin film, the incident x-ray path length decreases as α is increased. The value of the path length ($\underline{x}$) varies by:

$$x = t/\sin(\theta + \alpha) \tag{11}$$

where ($\underline{t}$) is the thickness of the sample in centimeters. Equation (10) may be rewritten

$$I_\alpha = \frac{I_o D}{(1 + M)\mu} [1 - e^{-(1+M)\mu t/\sin(\theta+\alpha)}] \tag{12}.$$

Again, at $\alpha = 0$, $\underline{M} = 1$ and $\sin(\theta + \alpha) = \sin\theta$, so that

$$I_{\alpha=0} = I_s = \frac{I_o D}{2\mu} [1 - e^{-2\mu t/\sin\theta}] \tag{13}$$

and

$$\frac{I_\alpha}{I_s} = \frac{2}{1 + M} \left[\frac{1 - e^{-(1+M)\mu \underline{t}/\sin(\theta+\alpha)}}{1 - e^{-2\mu t/\sin\theta}} \right] \tag{14}.$$

Equation (14) may be used in exactly the same manner as Equation (8) to determine relative intensities. An example of a plot of relative intensities versus angles of tilt for a typical film sample from this study is represented in Fig. 33. It is the slope from a plot such as Fig. 33 which represents the average particle orientation of a coating film.

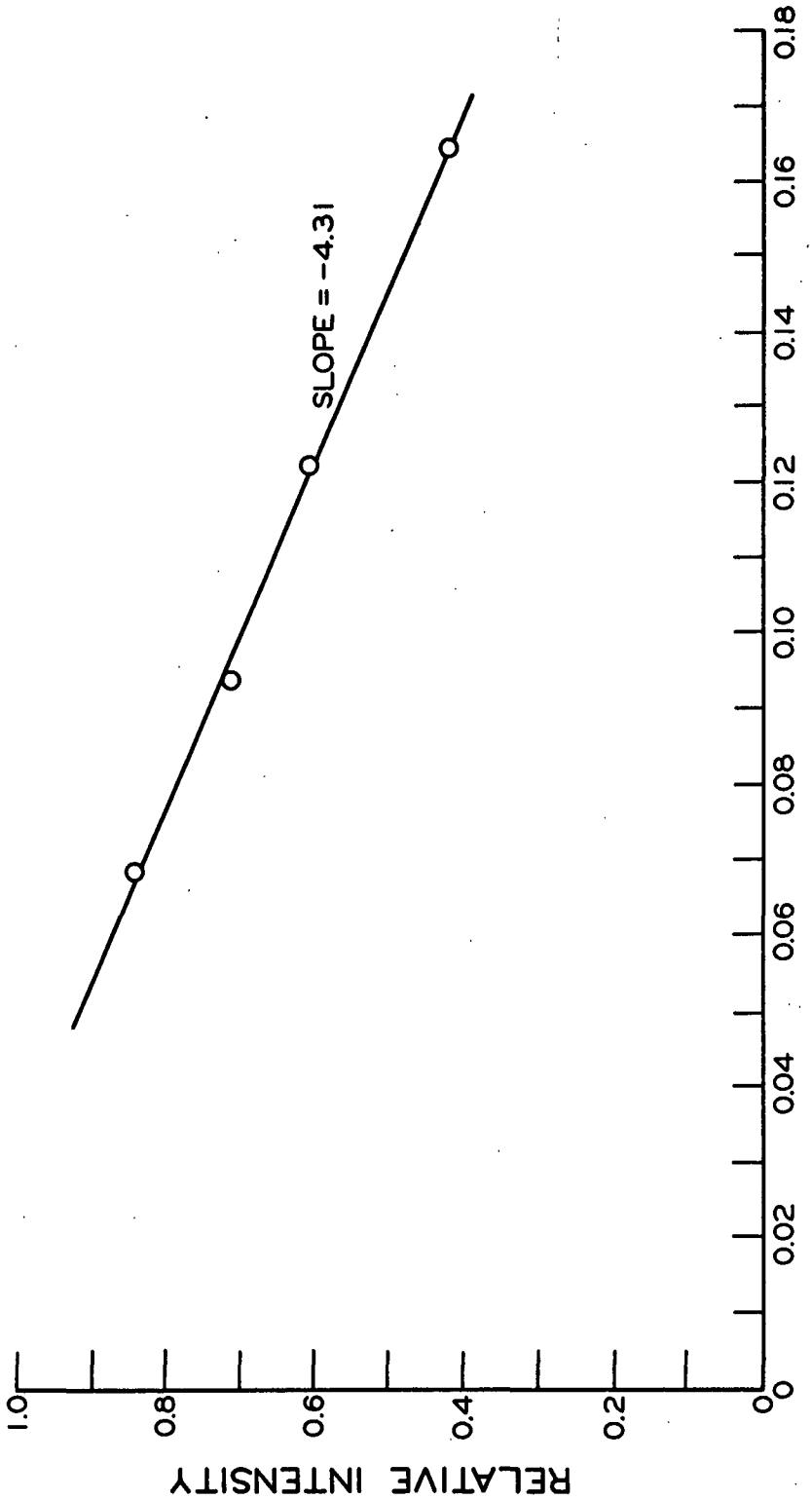

Figure 33. Example of a Plot from Which the Particle Orientation of a Coating Film is Determined; a Starch-Clay Sample of $f_{-p} = 0.6958$

FURTHER EVALUATIONS OF AND REFINEMENTS IN THE X-RAY DIFFRACTION TECHNIQUE FOR MEASURING FILM PARTICLE ORIENTATIONS

Kraske has shown that the mechanical aspects of the x-ray diffraction technique such as mounting samples and operating the x-ray unit are reproducible. Kraske also showed that the major difficulty in obtaining reproducibility in particle orientation determinations on coating films was due to the range of particle orientations existing within a given coating film. To obtain an average orientation for a coating film, Kraske used 4-ply composite samples. This was also done in this study.

In determining particle orientations in the manner used in the present study, two things are of considerable importance. First, individual pieces of film sample must not exhibit two-sidedness. The orientations measured must be an average over an entire film thickness to be of value. Secondly, the measured orientations of composite samples must represent a true average for the four pieces of sample. If composite samples exhibited large defocusing errors from the lower samples in the composite, then largely only the orientation of the top samples would be measured. Comparison of composites would then be just a comparison of the top samples of the composites, and the advantage of the composite would be lost.

The results shown in Table V represent an examination of film two-sidedness, and an estimate of the contribution to orientation values of the lower samples in a four-piece composite sample. The results are obvious except for an explanation of how the contribution of the lower samples in a composite was determined. A composite sample of a film was examined such that the top and bottom samples of a 2-ply composite were separated by an air space equivalent to two coating film thicknesses (indicated as wedged sample in Table V). The composite sample was then examined with the bottom piece of the coating film sample flush against the

top sample (indicated as unwedged in Table V). The results from the examination of the same bottom sample piece at different positions relative to the top sample gives an indication of whether or not the contribution of the samples in a composite is affected by their position relative to the top sample.

TABLE V

FILM PARTICLE ORIENTATION REPRODUCIBILITY, 4-POINT BASIS

Sample Designation, (f_p)	Orientation Slope (R.I. vs. α)
[a]0.9058 side no. 1	-3.22
0.9058 side no. 2	-3.08
0.9058 wedged	-3.00
0.9058 unwedged	-3.28

[a]Samples were from a starch-clay film formed on nonporous foil.

The results in Table V are satisfactory. These results indicate that the film samples do not exhibit excessive two-sidedness, and that the orientation values obtained for composite samples are averages which include the contribution of all of the four pieces in the composite.

The results in Table V were based upon four relative intensity points per sample, and all of the orientation results on starch-clay films on foil were based upon four relative intensity determinations per sample. During the study, it became apparent that determining film particle orientations by only four points was somewhat inefficient. A single bad point could greatly affect a film orientation determination. To improve the technique, an eight-point relative intensity basis was tried. It was found that the use of more relative intensity points appeared to give more reliable orientation results. This is illustrated in

Table VI. The data in Table VI show the reproducibility of an orientation determination on a coating film based on 8 relative intensity points as compared to the reproducibility of a film orientation value determined from 4 relative intensity points. The variation in particle orientation values between two composite samples from the same coating was less when the orientation determinations were based on 8 relative intensity points than when the orientation was based upon 4 relative intensity measurements.

TABLE VI

FILM PARTICLE ORIENTATION REPRODUCIBILITY, 8-POINT BASIS

No. of Relative Intensity Points Used in Determination	Sample Designation, f_{-p}	Orientation Slope
8[a]	0.9265	-2.48
8	0.9265	-2.51
4[b]	0.8928	-3.31
4	0.8928	-3.55

[a]The orientation values based upon eight relative intensity points were determined on samples from PVA-clay films formed on a nonporous substrate.

[b]The orientation values based upon four relative intensity points were determined by Kraske (3) on samples from starch-clay films formed on a porous substrate.

The orientations for the PVA-clay films, the latex-clay films, and the starch-clay films formed on a porous substrate were determined on the basis of 8 relative intensity points. Fewer films from a system had to be studied to establish trends in particle orientations with changing film adhesive contents because the reliability of each film orientation value was better than when only 4 relative intensity points were used to determine an orientation.

It should be pointed out that throughout this study a slit system of $1/4^{o}$ divergence slit – ∞ receiving slit – 4^{o} scatter slit was used. This slit system was determined experimentally to be the most satisfactory by Kraske. Kraske has presented a complete discussion of the advantages of this system in his thesis (3).

DETERMINATION OF SURFACE AREAS BY THE B.E.T. METHOD

The Brunauer, Emmett, and Teller (B.E.T.) equation (42) for the isothermal adsorption of an infinite number of molecular layers of a gas on a free surface may be expressed in the form:

$$\frac{P}{V(P_o - P)} = \frac{(c - 1)}{V_m c}\frac{P}{P_o} + \frac{1}{V_m c}$$

where

P = the equilibrium gas pressure,

P_o = the saturation vapor pressure of the adsorbate,

V = the volume of adsorbed gas (ml. S.T.P.) per gram of absorbent,

V_m = the volume of gas required to form a monolayer on the adsorbent surface, and

c = a dimensionless constant.

This equation is of the form $y = mx + b$. A plot of $P/V(P_o - P)$ versus P/P_o yields a straight line of slope $(c - 1)/V_m C$ and intercept $1/V_m C$. This equation is quite rigorous for relative pressures ranging from 0.05 to 0.30. The volume of gas corresponding to monolayer formation (V_m) can be obtained from the slope and intercept of the straight-line plot. Since the cross-sectional area of the absorbate molecule nitrogen is known, the area corresponding to V_m can be calculated. Kraske (3) has demonstrated the applicability and reliability of this method for determining surface areas of coatings.

DETERMINATION OF PORE DISTRIBUTIONS BY THE PIERCE METHOD

Pore distributions may be determined by interpreting gas adsorption-desorption isotherms in the high relative pressure range. The Pierce (46) treatment of isotherm interpretation was used in this study. Pierce's method is based upon the Kelvin equation:

$$\ln \frac{P}{P_o} = - \frac{2\upsilon M_v}{RTr}$$

where

P = gas pressure at equilibrium,

P_o = saturation vapor pressure of adsorbate,

υ = surface tension,

M_v = molar volume,

r = pore radius,

R = gas constant, and

T = absolute temperature.

The major assumptions which Pierce makes are: (1) that the pores are cylindrical, (2) that some form of the Kelvin equation is applicable for computing the pore radii from the relative pressures at which desorption occurs, and (3) the film thickness remaining on the pore walls after the inner capillary volume is desorbed is the same as that on a nonporous surface at the same relative pressure.

The arithmetic involved in calculating pore distributions is described completely by Pierce, and a further description here of the manipulations involved would serve no purpose. Kraske (3) has shown the reproducibility of the gas adsorption technique at high relative pressures when applied to coating samples.

Determinations of total pore volumes and complete pore size distributions by nitrogen gas adsorption were not possible in this study for the starch-clay

films formed on a nonporous substrate. For a complete estimate of the pore size distribution of a sample and its total pore volume, a complete adsorption-desorption isotherm must be obtained. A material having comparatively large pores yields an adsorption isotherm which approaches saturation asymptotically (80), and thus, a complete isotherm cannot be obtained. Blumenthal, Sourirajan, and Nobe (54) have shown the effect of pore size on the adsorption isotherm. It is impossible to saturate a sample, and obtain a complete adsorption-desorption isotherm within a reasonable time expenditure if the sample has large pores.

The asymptotic approach by the adsorption isotherm of a sample having large pores can be explained by the capillary condensation theory. According to the Kelvin equation, the relative pressure at which capillary condensation can take place increases exponentially with increases in pore size (54). Until a very high relative pressure is reached, large pores are not filled. At high relative pressures the adsorption isotherm rises rapidly or asymptotically with relative pressure. The practical limit in pore size for the complete determination of pore size distributions by gas adsorption is about 0.1 μ in radius. Beyond pore sizes of 0.1 μ in radius, samples are difficult if not impossible to saturate, and the various isotherm treatments for determining pore distribution, such as the Pierce method, do not hold.

An example of the shape of the adsorption isotherm of a sample containing large pores (and thus having an indeterminable saturation point and incomplete adsorption-desorption isotherm) is presented in Fig. 34. Also in Fig. 34 are shown the adsorption isotherms of the samples considered in this study. Obviously, they are of the same type, and it is impossible to obtain the void volumes or complete pore distributions of these samples.

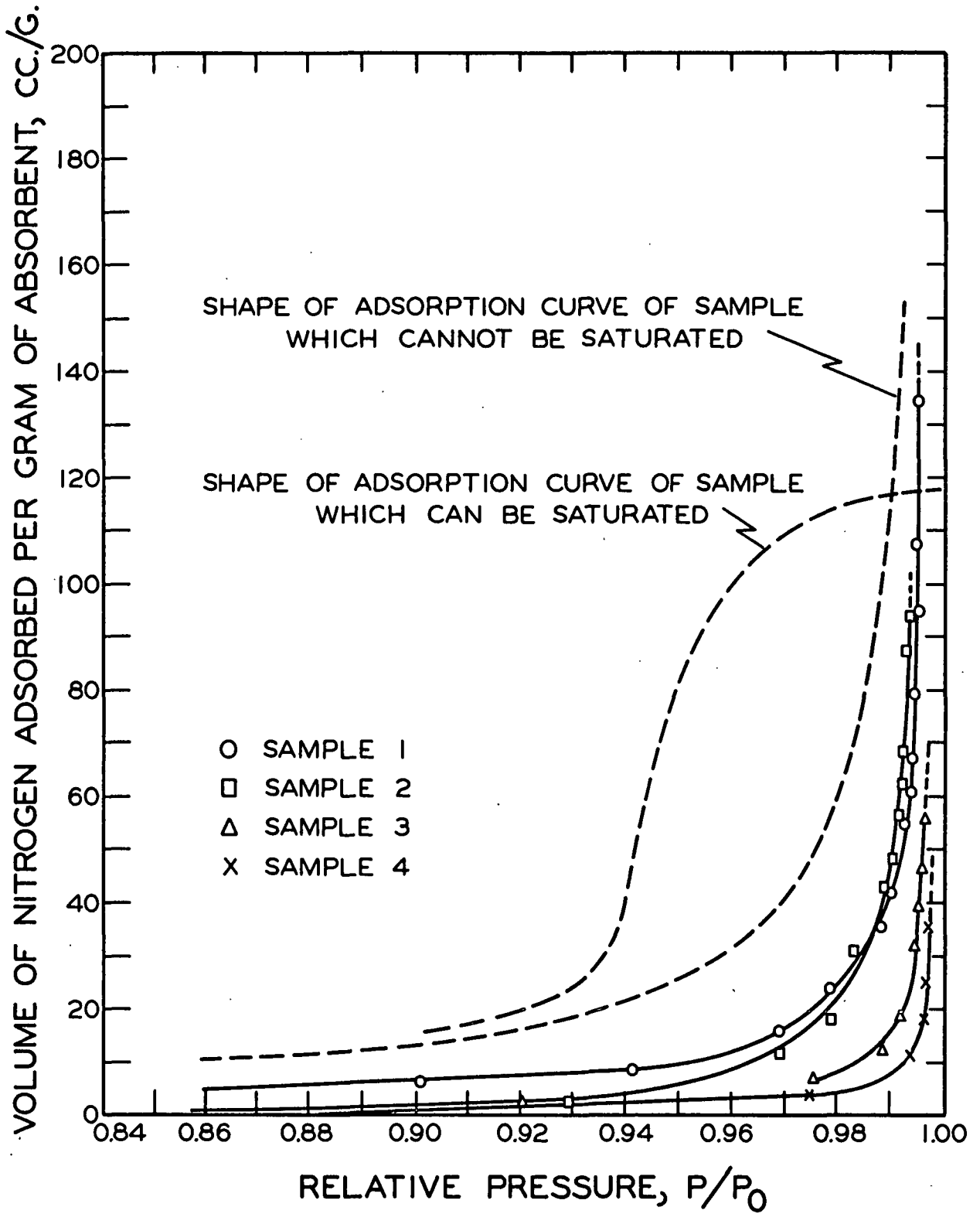

Figure 34. Nitrogen Gas Adsorption Isotherms for Selected Starch-Clay Film Samples

Although a complete pore distribution analysis was impossible, an attempt was made to analyze the changes in the smaller or measurable pores of the four coating samples under consideration in this study. The assumption was made that the partial desorption curve which was obtained was valid. This assumption is based on the phenomenon of scanning the hysteresis loop as proposed by Rao (81) and discussed by Brunauer (45). Briefly, scanning is the condition where if one starts from any point on the adsorption branch within the hysteresis region for a sample and reduces the pressure above a sample, the hysteresis loop is crossed and the desorption branch is reached. This point on the desorption branch and all subsequent desorption points are considered valid. Once one has assumed that scanning is valid, the partial desorption isotherm obtained can be treated by the usual theory.

There is some objection to assuming a valid desorption curve if a sample is not completely saturated. Barrett and Joyner (80) have presented results which indicate that there may be some slight deviations in the desorption curve obtained from a sample not completely saturated, as compared to the desorption curve obtained if the sample was saturated. However, these deviations seem quite small, and for samples with widely differing pore structures, at least a qualitative estimate of the differences in pore structures may be made.

The pore distribution results that were presented in Fig. 8 of the thesis were calculated based on the assumption that the scanning concept is valid. It was pointed out that the distributions presented represented less than 50% of the total pore volume. The majority of the pore volume was composed of pores too large to be analyzed, and pores so small that they were inaccessible to nitrogen. The treatment of only a portion of the total pore volume of a sample to obtain a pore distribution has been used by other workers. Mikhail, Copeland,

and Brunauer (82) have applied treatments to gas adsorption isotherms where they state that they are obtaining distributions for only 40 to 50% of the total pore volume. In some of the samples upon which they determined pore distributions, they state that up to 50% of the pore system was inaccessible to nitrogen, and in other cases, 35% of the pore system accessible to nitrogen consisted of pores larger in diameter than the pores covered by their analysis.

APPENDIX II
DATA ON STARCH-CLAY FILMS ON A NONPOROUS SUBSTRATE

TABLE VII

DENSITIES OF STARCH-CLAY FILMS FORMED ON A NONPOROUS SUBSTRATE

Pigment Weight Fraction, f_p	Clay, Wt., g.	Starch Wt., g.	St./Clay Ratio	Film Area, $cm.^2$	Film Thickness, μ	Density, g./cc.	Film Sp. Volume v_f, cc./g.
1.0000	0.05205	0.0000	0.0000	3.496	110.58	1.347	0.7423
1.0000	0.05330	0.0000	0.0000	3.036	133.27	1.318	0.7587
0.9670	0.01612	0.00055	0.0341	3.177	42.53	1.234	0.8104
0.9620	0.01342	0.00053	0.0394	3.355	35.44	1.174	0.8518
0.9565	0.01078	0.00049	0.0454	3.236	31.20	1.115	0.8969
0.9409	0.03279	0.00206	0.0628	5.802	51.13	1.131	0.8842
0.9401	0.01200	0.00076	0.0633	3.485	33.68	1.087	0.9200
0.9274	0.00920	0.00072	0.0782	2.658	36.84	1.013	0.9872
0.9058	0.02269	0.00236	0.1040	5.636	41.71	1.067	0.9372
0.8918	0.01796	0.00218	0.1214	5.375	35.34	1.061	0.9425
0.8866	0.01102	0.00141	0.1279	3.093	37.72	1.066	0.9381
0.8572	0.01303	0.00217	0.1665	3.773	37.65	1.070	0.9345
0.8451	0.01593	0.00292	0.1833	5.367	32.39	1.065	0.9390
0.8221	0.00989	0.00214	0.2164	5.279	20.95	1.088	0.9191
0.8169	0.02035	0.00436	0.2241	5.412	37.62	1.223	0.8177
0.8036	0.01988	0.00486	0.2245	5.554	35.43	1.256	0.7962
0.7900	0.01305	0.00347	0.2659	3.724	33.59	1.322	0.7564
0.7756	0.02167	0.00627	0.2893	5.668	36.60	1.347	0.7424
0.7589	0.01901	0.00604	0.3177	5.616	32.27	1.382	0.7236
0.7439	0.02242	0.00772	0.3443	5.139	32.49	1.807	0.5534
0.7361	0.01057	0.00379	0.3585	3.332	24.55	1.756	0.5695
0.7134	0.01095	0.00440	0.4018	3.328	22.85	2.018	0.4955
0.6958	0.01313	0.00574	0.43717	3.361	26.79	2.094	0.4776
0.6730	0.00986	0.00479	0.48580	3.222	23.68	1.921	0.5206
0.4281	0.01995	0.02665	1.3360	6.000	43.14	1.801	0.5553
0.2398	0.00980	0.03107	3.1700	6.225	40.69	1.615	0.6192
0.0000	0.00000	0.03267		5.917	37.15	1.486	0.6729

TABLE VIII

AVERAGE PARTICLE ORIENTATIONS OF STARCH-CLAY FILMS FORMED ON A NONPOROUS SUBSTRATE

Film Designation, (f_p)	Orientation Slope, (R.I. vs. α)	Correlation Coefficient
0.96701	-2.98	-0.9819
0.96201	-4.09	-0.9945
0.95652	-3.52	-0.9173
0.9401	-3.45	-0.9968
0.9274	-3.99	-0.9915
0.9058	-3.03	-0.9890
0.8918	-2.45	-0.9339
0.8866	-3.14	-0.9781
0.8572	-3.02	-0.9928
0.8451	-2.81	-0.9974
0.8169	-3.45	-0.9883
0.8036	-3.36	-0.9959
0.7756	-3.94	-0.9870
0.7589	-3.21	-0.9962
0.7900	-3.13	-0.9678
0.7439	-3.85	-0.9948
0.6958	-4.31	-0.9978
0.6730	-3.20	-0.9991

TABLE IX

RELATIVE INTENSITY AND ANGLE α DATA ON INDIVIDUAL STARCH-CLAY FILMS FORMED ON A NONPOROUS SUBSTRATE

Sample Designation, f_{-p}	Angle of Tilt, α, in degrees	Corrected Relative Intensity
0.9670	3.735	0.9046
	5.540	0.8531
	7.181	0.7148
	9.213	0.6426
0.9620	4.275	0.8272
	6.085	0.6642
	7.549	0.5829
	9.399	0.4632
0.9565	4.094	0.9004
	5.903	0.7460
	8.286	0.6085
	9.213	0.5876
0.9401	2.844	0.9184
	4.815	0.8256
	6.815	0.7101
	8.286	0.6057
0.9274	1.938	0.9441
	3.375	0.8383
	5.725	0.7558
	10.708	0.3417
0.9058	4.091	0.8824
	5.358	0.8163
	8.658	0.6077
	10.908	0.5501
0.8918	4.997	0.8910
	8.658	0.6616
	11.088	0.5497
0.8866	2.658	0.9149
	5.725	0.8261
	8.475	0.7691
	9.591	0.6003
0.8572	3.375	0.9821
	6.085	0.8756
	9.028	0.6813
	11.088	0.6189
0.8451	2.482	0.9438
	4.275	0.8751
	6.267	0.7910
	8.471	0.6743

TABLE IX (Continued)

RELATIVE INTENSITY AND ANGLE α DATA ON INDIVIDUAL STARCH-CLAY FILMS FORMED ON A NONPOROUS SUBSTRATE

Sample Designation, f_{-p}	Angle of Tilt, α, in degrees	Corrected Relative Intensity
0.8169	4.275	0.8543
	5.903	0.7981
	7.181	0.6824
	9.028	0.5879
0.8036	3.196	0.8899
	4.996	0.7883
	7.733	0.6620
	9.958	0.4968
0.7900	4.455	0.9780
	5.358	0.8562
	7.733	0.7827
	9.213	0.7024
0.7756	3.735	0.8261
	6.267	0.7184
	7.917	0.5538
	9.591	0.4401
0.7589	3.735	0.8545
	6.085	0.7520
	7.549	0.6441
	10.527	0.5118
0.7439	4.094	0.8037
	6.085	0.7010
	7.733	0.5475
	10.335	0.3976
0.6958	3.915	0.8425
	5.358	0.7082
	6.998	0.6086
	9.399	0.4206
0.6730	4.094	0.9603
	5.725	0.8854
	8.102	0.7454
	10.150	0.6294

TABLE X

GAS ADSORPTION DATA

Starch-Clay Film, f_p = 0.9565

B.E.T. Data			Desorption Data for Pore Distributions		
P, mm. Hg	P/P_o	V Adsorbed/g., cc./g.	P, mm. Hg	P/P_o	V Adsorbed/g., cc./g.
67.6	0.089	1.223	752.4	0.9955	94.02
112.3	0.148	1.491	750.1	0.9951	91.15
162.6	0.214	1.720	748.4	0.9931	88.58
221.4	0.292	1.933	747.9	0.9924	83.99
			747.8	0.9914	77.51
			748.7	0.9906	68.16
			747.4	0.9871	57.05
			747.9	0.9846	46.31
			744.9	0.9790	34.46
			738.1	0.9689	23.84
			724.7	0.9513	13.54
			646.1	0.8469	5.48
Starch-Clay Film, f_p = 0.9058 ✓					
68.6	0.089	0.964	759.3	0.9971	128.08
114.4	0.148	1.146	756.1	0.9942	119.00
165.1	0.213	1.305	751.3	0.9895	99.38
224.0	0.289	1.449	751.3	0.9884	90.55
			749.1	0.9864	78.91
			747.5	0.9852	69.05
			744.4	0.9819	56.46
			742.5	0.9794	41.71
			732.8	0.9678	27.49
			727.6	0.9609	18.85
			699.4	0.9253	6.60
			565.5	0.7486	2.50
Starch-Clay Film, f_p = 0.8572					
79.1	0.102	0.532	750.8	0.9973	39.56
129.7	0.167	0.770	747.9	0.9942	30.54
186.5	0.240	0.910	744.3	0.9894	19.93
252.3	0.325	1.015 ✓	734.7	0.9765	8.31
			670.7	0.8914	5.20
Starch-Clay Films, f_p = 0.8036					
78.0	0.102	0.430	752.7	0.9967	24.72
139.2	0.181	0.452	746.6	0.9898	17.04
200.6	0.261	0.565	754.3	0.9887	12.98
270.3	0.351	0.750	737.0	0.9791	6.91
			723.2	0.9611	2.70
			685.6	0.9128	1.12
				0.8565	

APPENDIX III
DATA ON PVA-CLAY FILMS

TABLE XI

DENSITIES OF PVA-CLAY FILMS

Pigment Weight Fraction, f_p	Clay Wt., g.	PVA Wt., g.	PVA/Clay	Film Area, $cm.^2$	Film Thickness, μ	Density, g./cc.	Film Sp. Volume, v_f, cc./g
0.9782	0.01529	0.00034	0.0222	3.284	41.53	1.151	0.869
0.9664	0.01465	0.00051	0.0348	3.401	36.12	1.193	0.838
0.9265	0.01387	0.00110	0.0793	3.646	32.31	1.263	0.792
0.8586	0.01148	0.00189	0.1646	3.401	25.98	1.513	0.661
0.8313	0.01587	0.00322	0.2029	3.373	35.85	1.579	0.633
0.8046	0.01491	0.00362	0.2428	3.494	31.15	1.701	0.588
0.7940	0.01546	0.00401	0.2594	3.459	32.39	1.738	0.575
0.7680	0.01437	0.00434	0.3020	2.456	28.92	1.871	0.535
0.7621	0.01384	0.00432	0.3120	3.424	27.97	1.895	0.528
0.6873	0.01046	0.00476	0.4551	3.455	23.21	1.900	0.526
0.4121	0.00539	0.00769	1.4270	3.391	24.67	1.569	0.637

TABLE XII

AVERAGE PARTICLE ORIENTATIONS OF PVA-CLAY FILMS FORMED ON A NONPOROUS SUBSTRATE

Film Designation, f_p	Orientation Slope, R.I. vs. α	Correlation Coefficient
0.9782	-2.58	-0.9809
0.9265	-2.48, -2.51[a]	-0.9917, -0.9945
0.8313	-2.43	-0.9757
0.8046	-2.56	-0.9852
0.7680	-2.53	-0.9935
0.6873	-2.77	-0.9864

[a] Duplicate sample from the same film.

TABLE XIII

RELATIVE INTENSITY AND ANGLE α DATA ON INDIVIDUAL PVA-CLAY FILMS FORMED ON A NONPOROUS SUBSTRATE

Sample Designation, f_{-p}	Angle of Tilt, α, in degrees	Corrected Relative Intensity
0.9782	2.126	0.9359
	3.376	0.9130
	4.454	0.8387
	5.725	0.8455
	7.549	0.7441
	9.399	0.6201
	9.958	0.5588
	12.036	0.5309
0.9265	1.415	0.9502
	2.304	0.9398
	3.376	0.9009
	5.725	0.7880
	7.181	0.7167
	8.286	0.6533
	9.586	0.5792
	12.036	0.5358
0.9265 (duplicate)	1.593	0.9348
	4.091	0.8217
	5.725	0.7777
	6.632	0.7107
	7.733	0.7014
	9.399	0.5994
	10.899	0.5124
	11.846	0.4966
0.8313	1.948	0.9317
	3.376	0.9209
	4.635	0.8982
	6.449	0.8275
	7.733	0.7676
	9.586	0.6647
	10.899	0.6059
	11.656	0.5225
0.8046	2.661	0.9618
	3.735	0.8807
	4.815	0.8797
	6.267	0.8321
	7.733	0.7407
	8.841	0.7140
	9.958	0.6432
	11.466	0.5367

TABLE XIII (Continued)

RELATIVE INTENSITY AND ANGLE α DATA ON INDIVIDUAL PVA-CLAY FILMS FORMED ON A NONPOROUS SUBSTRATE

Sample Designation, f_p	Angle of Tilt, α, in degrees	Corrected Relative Intensity
0.7680	1.593	0.9752
	3.196	0.9549
	5.177	0.8468
	6.998	0.7736
	8.102	0.7289
	9.027	0.6977
	10.335	0.6138
	11.466	0.5481
0.6873	1.948	0.9558
	3.915	0.8977
	5.358	0.8638
	6.267	0.8122
	7.733	0.7423
	8.471	0.6701
	10.335	0.6004
	12.417	0.4565

APPENDIX IV
DATA ON LATEX-CLAY FILMS

TABLE XIV

DENSITIES OF LATEX-CLAY FILMS FORMED ON A NONPOROUS SUBSTRATE

Pigment Weight Fraction, f_p	Clay Wt., g.	Latex Wt., g.	Latex/Clay	Film Area, $cm.^2$	Film Thickness, μ	Density, g./cc.	Film Sp. Volume, v_f, cc./g.
0.9444	0.01545	0.00091	0.0589	3.069	39.48	1.350	0.742
0.9049	0.02312	0.00243	0.1051	3.689	50.23	1.380	0.725
0.8746	0.01346	0.00193	0.1434	3.184	34.35	1.406	0.712
0.8098	0.01418	0.00333	0.2348	3.504	34.97	1.430	0.699
0.7555	0.01557	0.00504	0.3237	3.711	35.25	1.575	0.635

TABLE XV

AVERAGE PARTICLE ORIENTATIONS OF LATEX-CLAY FILMS FORMED ON A NONPOROUS SUBSTRATE

Film Designation, f_p	Orientation Slope, R.I. vs. α	Correlation Coefficient
0.9444	-2.58	-0.9731
0.9049	-3.17	-0.9861
0.8746	-3.39	-0.9665
0.7555	-3.88	-0.9936

TABLE XVI

RELATIVE INTENSITY AND ANGLE α DATA ON INDIVIDUAL LATEX-CLAY FILMS FORMED ON A NONPOROUS SUBSTRATE

Sample Designation, f_p	Angle of Tilt, α, in degrees	Corrected Relative Intensity
0.9444	0.875	0.9863
	2.661	0.9743
	3.735	0.9394
	5.358	0.8890
	7.549	0.7795
	8.471	0.7147
	9.773	0.6458
	11.088	0.5315
0.9049	2.126	0.9058
	3.555	0.8700
	4.996	0.7419
	6.998	0.5964
	7.917	0.5327
	9.958	0.4967
	10.708	0.4253
	12.036	0.3847
0.8746	0.705	0.9980
	2.661	1.0046
	3.735	0.9365
	5.177	0.8766
	7.365	0.7769
	8.658	0.6284
	9.773	0.5039
	11.277	0.4205
0.7555	2.308	0.9588
	3.915	0.8778
	5.177	0.8184
	6.267	0.6830
	0.286	0.6056
	9.028	0.4911
	10.708	0.4231
	12.036	0.3090

APPENDIX V
DATA ON STARCH-CLAY FILMS ON A POROUS SUBSTRATE

TABLE XVII

DENSITIES OF STARCH-CLAY FILMS FORMED ON A POROUS SUBSTRATE

Pigment Weight Fraction, f_p	Clay Wt., g.	Starch Wt., g.	Starch/Clay	Film Area, $cm.^2$	Film Thickness, μ	Density, g./cc.	Film Sp. Volume, v_f, cc./g.
1.0000	0.04032	0.0000	0.0000	6.630	43.05	1.412	0.709
0.9533	0.00653	0.00032	0.0490	1.727	28.84	1.377	0.726
0.9336	0.01110	0.00079	0.0712	3.243	26.17	1.402	0.713
0.9036	0.01219	0.00130	0.1067	3.268	28.62	1.443	0.693
0.8675	0.01316	0.00201	0.1527	3.093	33.84	1.451	0.689
0.8512	0.01510	0.00264	0.1748	3.358	35.50	1.487	0.673
0.8293	0.01462	0.00301	0.2059	3.469	33.48	1.517	0.659
0.8061	0.01243	0.00299	0.2405	3.089	31.91	1.564	0.639
0.7756	0.01358	0.00393	0.2894	3.401	31.48	1.636	0.611
0.7446	0.01449	0.00497	0.3430	3.225	35.93	1.678	0.596
0.7187	0.01676	0.00656	0.3914	3.313	37.07	1.889	0.529
0.6992	0.01513	0.00651	0.4303	3.108	35.04	1.986	0.504
0.4479	0.00932	0.01149	1.2328	3.188	36.66	1.781	0.561

TABLE XVIII

AVERAGE PARTICLE ORIENTATIONS OF STARCH-CLAY FILMS FORMED ON A POROUS SUBSTRATE

Film Designation, f_p	Orientation Slope, R.I. *vs.* α	Correlation Coefficient
0.9336	-3.48	-0.9946
0.9036	-3.30	-0.9969
0.8675	-2.65	-0.9885
0.8293	-2.71	-0.9746
0.7756	-3.22	-0.9668
0.7187	-3.39	-0.9924

TABLE XIX

RELATIVE INTENSITY AND ANGLE α DATA ON INDIVIDUAL STARCH-CLAY FILMS FORMED ON A PORous SUBSTRATE

Sample Designation, f_{-p}	Angle of Tilt, α, in degrees	Corrected Relative Intensity
0.9336	1.774	0.9819
	2.479	0.9253
	4.105	0.8861
	5.919	0.8262
	7.750	0.7319
	9.054	0.6189
	10.558	0.5316
	11.887	0.4280
0.9036	2.129	0.9802
	3.023	0.9293
	3.921	0.8966
	5.550	0.8195
	7.012	0.7221
	7.749	0.6754
	9.420	0.5794
	11.113	0.4565
0.8675	1.415	0.9907
	3.197	0.9718
	4.815	0.9062
	6.267	0.8050
	8.102	0.7270
	9.399	0.6662
	10.771	0.6155
	11.466	0.5341
0.8293	1.774	0.9885
	2.479	0.9586
	3.924	0.8924
	5.550	0.8957
	7.012	0.8016
	7.941	0.7336
	9.430	0.6243
	10.558	0.5630
0.7756	0.245	0.9150
	2.126	0.9670
	3.197	0.8894
	4.454	0.8171
	6.267	0.6804
	7.917	0.6099
	8.993	0.5091
	10.335	0.4032